Rayonier Mill Off-Property Soil Dioxin Study

Final Project Report, Public Review Draft

Prepared for

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List of Acronyms and Abbreviations

2,3,7,8-TCDD	2,3,7,8-tetrachlorodibenzo-*p*-dioxin
ALS	alternating least squares
ARI	Analytical Resources Inc.
Axys	Axys Analytical Services Ltd.
CCME	Canadian Council of Ministers of the Environment
CSM	Conceptual Site Model
DAHP	[Washington] Department of Archaeology and Historic Preservation
dioxins	polychlorinated dibenzo-*p*-dioxins
DL	detection limit
E & E	Ecology and Environment, Inc.
Ecology	Washington State Department of Ecology
EDL	estimated detection limit
EIM	Environmental Information Management
EMPC	estimated maximum possible concentrations
EPA	[U.S.] Environmental Protection Agency
FALCON	[EPA's] Fingerprint Analysis of Contaminant Data
FWEC	Foster Wheeler Environmental Corporation
furans	polychlorinated dibenzofurans
HCA	hierarchical cluster analysis
HEC	Herrera Environmental Consultants
HFB	hog fuel boiler
HLA	Harding Lawson Associates
HpCDD	heptachlorodibenzo-*p*-dioxin
HpCDF	heptachlorodibenzofuran
HxCDD	hexachlorodibenzo-*p*-dioxin
HxCDF	hexachlorodibenzofuran
ITT	International Telephone and Telegraph
LEKT	Lower Elwha Klallam Tribe
MCDD	monochlorodibenzo-*p*-dioxin
MCDF	monochlorodibenzofuran
MDL	method detection limit
mg	milligrams
MPE	Malcolm Pirnie Engineers
MTCA	[Washington's] Model Toxics Control Act
ND	nondetect (same meaning as lab code "U")
ng/kg	nanograms per kilogram
NGVD	National Geodetic Vertical Datum
OCDD	octachlorodibenzo-*p*-dioxin
OCDF	octachlorodibenzofuran
PCDD	polychlorinated dibenzo-*p*-dioxin
PCDF	polychlorinated dibenzofuran
PCA	principal components analysis
PeCDD	pentachlorodibenzo-*p*-dioxin

PeCDF	pentachlorodibenzofuran
ppt	parts per trillion
SDL	sample-specific detection limit
SQAP	Sampling and Quality Assurance Plan
SSP	Soil Sampling Plan
TCDD	tetrachlorodibenzo-*p*-dioxin
TCDF	tetrachlorodibenzofuran
TEF	toxicity equivalency factor
TEQ	toxic equivalent concentration
TOC	total organic carbon
WAC	Washington Administrative Code
WDOT	Washington Department of Transportation

Executive Summary

ES-1 Introduction

The Washington State Department of Ecology (Ecology) initiated the *Rayonier Mill Off-Property Soil Dioxin Study* to increase understanding of polychlorinated dibenzo-*p*-dioxin (dioxin) and polychlorinated dibenzofuran (furan) soil contamination in areas surrounding the former Rayonier Mill. Dioxins and furans were emitted from the former Port Angeles Rayonier Mill during decades of pulp and paper production and potentially deposited on soils surrounding the mill. In particular, the emissions came from a hog fuel boiler (HFB) that burned salt-laden wood, a process that produces dioxins and furans. Areas outside the former mill property boundary are referred to as “off-property” and are the focus for this study.

The former Rayonier Mill has been designated as a site for cleanup actions under Washington’s Model Toxics Control Act (MTCA). Ecology has not yet determined the full extent of the site. Ecology is investigating whether areas beyond the property boundaries (“off-property” areas) have been impacted by mill emissions.

Planning for the study began in February 2008 with development of the *Conceptual Site Model* (CSM) report (E & E 2008a). This report identifies possible sources of dioxins/furans and discusses the many factors that influence how and where dioxins/furans could be deposited after being released to the air.

Following development of the CSM report, Ecology met with interested parties, including the Lower Elwha Klallam Tribe (LEKT), City of Port Angeles, Clallam County Health Department, Washington Department of Health, and Olympic Environmental Council, to obtain input on the study objectives.

ES-2 Study Objectives and Design

In any given area, dioxin/furan concentrations measured in soil may vary greatly and typically are attributable to multiple sources. This is particularly true in urban environments, where contributions are from a combination of point sources (e.g., incinerators, boilers), diffuse sources (e.g., forest and house fires, automobiles), and property-specific sources (e.g., chemical applications, ash disposal, burn barrels). For this reason, determining the specific source of measured dioxins/furans in soils is a challenging problem. The overarching goal of this study is to increase understanding of dioxin/furan soil contamination in areas surrounding the former Rayonier Mill, including the magnitude and likely sources of contamination of surface soils.

Specific study objectives include:

- Determine the magnitude of dioxin/furan contamination in off-property surface soils potentially impacted by airborne emissions from the former Rayonier Mill, and

- Determine the relative contribution to measured soil dioxin/furan concentrations of former Rayonier Mill emissions compared with contributions from other potential sources.[1]

A detailed discussion of the study objectives, including issues outside the scope of the study, is provided in the *Soil Sampling Plan* (SSP; E & E 2008b).

The rationale for defining the boundary for this soil dioxin study area, as well as for determining sample density and locations, is also discussed in the SSP. The physical and chemical information on dioxins/furans in the environment and factors influencing their deposition on surrounding soils, as discussed in the CSM, provides a basis for design of the soil study. In addition, the design considers factors such as topography, meteorology and previous air modeling and monitoring reports, locations of citizen-reported odors associated with the former mill during operation, existing land cover, history of land disturbances, and knowledge gained from dioxin/furan studies conducted in other areas.

The SSP was released for public review in July 2008, during which time Ecology held an open house and technical workshop in Port Angeles to explain the study design and solicit comments on the proposed design. The final SSP report was issued, inclusive of public comments, in September 2008.

ES-3 Study Implementation

The specific sample location selection criteria, protocol for sample collection, and quality assurance and quality control criteria are provided in the *Sampling and Quality Assurance Plan* (SQAP; E & E 2008c). The SQAP also includes a protocol for cultural resources monitoring, health and safety planning, methods for recruiting volunteers, and general data analysis and reporting guidelines.

Recruitment of volunteers for participation in the soil sampling program began in August 2008 and continued through the duration of the field sampling event. Field sampling teams collected 85 soil samples in September and November 2008. The goal of 100 soil samples was not reached due to a lack of volunteers and lack of properties meeting selection criteria.

Soil samples were submitted for analysis of dioxins/furans and total organic carbon (TOC). All results were obtained from the analytical laboratories in December 2008 and were validated by a third-party firm, as prescribed in the SQAP. E & E received the fully validated database and data usability report in January 2009.

ES-4 Data Reporting

Ecology provided individual sample results to volunteer property owners in February 2009. The full database also was uploaded to Ecology's Environmental Information Management System

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[1] In evaluating the relative contribution of former Rayonier Mill emissions versus other sources, it is not the objective of this study to perform detailed quantitative allocations among potential sources or to apportion liability or responsibilities among potentially liable parties. The former Rayonier Mill is recognized as being one of several locations in Port Angeles that historically burned salt-laden wood.

(EIM), which is accessible to the public. However, personal identifiers such as the property owner name, address, and contact information were not included with the sample location information.

Dioxins and furans are families of chemical compounds with related structures. Only 17 distinct dioxin/furan compounds are typically evaluated; each distinct form is called a "congener." Concentrations of each congener are typically reported as toxic equivalent concentrations (TEQs), meaning they have been adjusted to reflect their potency relative to one of the most toxic congeners.

A general overview of the sample results is included in the document *Data Summary Technical Memorandum* (E & E 2009), which was released in February 2009. The memorandum does not interpret the data, but it does provide the raw data as well as TEQs of dioxins/furans, fractional contribution of individual dioxin/furan compounds, and graphical representations of the data (histograms, line plots, scatter plots). Maps showing approximate sample locations and dioxin/furan concentrations also are included. As for the EIM, volunteer property owner identification information is not included in the report.

ES-5 Data Evaluation

Following release of the data to study volunteers and the general public, Ecology initiated data evaluation, which included detailed consideration of data with respect to the study objectives and is the subject of this final project report.

In this study, 85 surface soil samples (0 to 3 inches) were collected in and near Port Angeles, Washington, to characterize dioxin/furan concentrations and patterns in off-property areas around the former Rayonier mill. Almost half of those samples (40 of 85) were found to have total TEQ concentrations greater than the MTCA Method B direct contact value of 11.1 nanograms TEQ per kilogram (ng TEQ/kg).[2]

A primary objective of the study was to evaluate sources and their relative contributions to measured soil TEQ concentrations. Data evaluations addressed four lines of evidence:

- Magnitude
- Spatial Pattern
- Chemical Pattern
- Mass Balance

Multivariate chemometric analyses (unmixing analyses) of the soil dioxin/furan dataset played an important role in source evaluations. Once unmixing analyses of the TEQ profiles of soil samples partitioned total TEQ into separate source-related increments, the initial evaluations of

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[2] The soil TEQ concentration equivalent to a 1 in 1,000,000 cancer risk from direct contact (incidental ingestion), calculated using the standard MTCA Method B equation for unrestricted (e.g., residential) land use, is 11.1 ng TEQ/kg. Throughout this report this will be referenced as the Method B value, which is used only as one point of comparison. Soil dioxin cleanup levels under MTCA are determined by Ecology later in the site cleanup process, and may reflect evaluations beyond direct contact exposure pathways and the default risk equation.

magnitude and spatial pattern based on total TEQ results were refined by considering source increments. Those source increment results were also used in an initial mass balance evaluation.

The evaluations for each line of evidence are summarized below.

TEQ magnitude summary. The approach and conclusions for the evaluation of the total TEQ results for Port Angeles soil samples are summarized as follows:

- Total TEQ results were variable, ranging from 0.80 to 76.3 ng TEQ/kg.
- A small number of high outlier TEQ concentrations occurred, consistent with observations in other soil dioxin studies.
- TEQ concentrations in the most rural portion of the soil dioxins/furans study area—the upslope transects—were far lower than in the developed urban areas of Port Angeles.
- Almost half (40 of 85) of the samples had TEQ values exceeding Ecology's Method B value of 11.1 ng TEQ/kg, including 33 of 60 grid-type samples.
- TEQ comparisons across sample types are affected by differences in the sampled areas for each type. Upslope transect and roadside-type samples in this study had lower median TEQ concentrations than grid and forest sample types.
- Although median TEQs were similar for grid- and forest-type sample subgroups, forest-type samples included a number of the higher TEQ results. Elevated TEQs in forest soils (a consequence of land cover) are consistent with the site conceptual model, especially given the locations of most forest-type samples well outside the Port Angeles urban core.
- Compared with available soil dioxin results from other locations, which are reasonably consistent with one another, soil dioxin TEQs in Port Angeles appear to be shifted higher. This suggests that one or more local sources may have contributed to moderately elevated soil TEQs.
- TEQs for the upslope transect-type samples, well outside the developed Port Angeles area, are similar to Washington statewide and U.S. rural sampling results.

Total TEQ spatial pattern summary. The approach and conclusions for the evaluation of spatial patterns of soil dioxins based on total TEQ concentrations are summarized as follows:

- Distance and distance/direction versus TEQ scatter plots (one-dimensional) and a dot map (two-dimensional) were used to evaluate spatial patterns for total TEQ results.
- The expected difference in total TEQ concentrations between urban and rural areas was confirmed, with markedly lower values for the upslope transect locations compared with urbanized areas of Port Angeles, and generally lower values in the less-developed easternmost sampling areas.
- Apart from the urban-to-rural gradient, no simple gradients or trends were evident for total TEQs within the urban portion of the study area, even if the evaluation was limited to only grid-type samples (n = 60) to reduce potential confounding from multiple sample types.

- Instances of high local variability in total TEQs for closely spaced sampling locations occurred, consistent with the conceptual model of comparatively high variability in developed areas where soil-disturbing activities and property-specific dioxin sources are likely.
- A few high-outlier total TEQ results appear anomalous compared with other nearby sampling locations.
- Grid-type sampling locations that exceed the MTCA Method B value of 11.1 ng TEQ/kg are widespread in developed areas of Port Angeles.
- The absence of clear spatial patterns in total TEQs that can be related to any single dioxin emissions source is influenced by the contributions from multiple dioxin sources across Port Angeles, as well as by varying individual property histories (soil-disturbing activities that dilute or reduce accumulated soil dioxin levels, and property-specific dioxin sources).

Unmixing analysis summary. The approach and conclusions for the multivariate evaluations of chemical patterns in the Port Angeles soil samples (unmixing analyses) are summarized as follows:

- Normalized TEQ profiles for the soil samples were developed as the basis for unmixing analyses, which used multivariate PCA and ALS techniques.
- PCA analyses and additional outlier detection methods identified 2 samples with unusual TEQ profiles; unmixing analyses were based on the remaining 83 samples.
- Three sources were determined sufficient to account for almost all (99.7%) of the variance in TEQ profiles across samples.
- The final unmixing model provided distinct TEQ profiles for each of 3 sources.
- The fractional contributions of each source profile to each soil sample were determined by the unmixing analyses, for all 85 samples (including 2 outliers); these results provide a partitioning, or decomposition, of total TEQs for samples into portions contributed by separate source profiles.
- Comparing the unmixing model TEQ profiles to measured TEQ profiles, the differences (residuals, for each congener contributing to TEQ) are small, demonstrating a high degree of goodness-of-fit for the model results.
- Interpretations of the 3 source profiles from unmixing analyses included compilation and review of a large number of characteristic source profiles, among which were numerous stack test results from HFBs burning salt-laden wood.
- Source 1, dominated by a single congener (2,3,7,8-TCDD), is similar to a tire burning profile and the TEQ profile for incidental dioxin formation during 2,4,5-T production.
- Source 2 is similar to a composite urban dioxins TEQ profile, including vehicle emissions; it is also similar to some HFB profiles, and may reflect a composite profile to some degree due to widespread co-occurrence of both typical urban and HFB sources in Port Angeles.

- Source 3 has strong similarity to the TEQ profile for stack emissions from a HFB burning salt-laden wood.

Source increment magnitude summary. The approach and conclusions for the evaluation of source increments for Port Angeles soil samples are summarized as follows:

- The unmixing model results were used to calculate TEQ increments from each of three source profiles for each of the 85 soil samples.
- Source 3 has a large contribution to total TEQ for many of the sampled locations; for grid-type samples, subtracting the Source 3 increments reduces the median TEQ by almost 60%.
- After subtracting Source 3 increments for grid-type samples, the remaining sample TEQs (sum of contributions from Sources 1 and 2) are similar to total TEQ results from other studies of urban soils; including Source 3 increments, the distribution of grid-type samples appears shifted higher compared to other studies of urban soils.
- After subtracting Source 3 increments for grid-type samples, remaining TEQs greater than 10 ng TEQ/kg are dominated by Source 1 contributions (10 of 11 cases); all Source 2 increments for grid-type samples are less than 9.7 ng TEQ/kg, with 47 out of 60 (78%) less than 5 ng TEQ/kg.
- Source 3 dominates most forest-type samples (greater than 70% contribution for 11 of 14 samples). After subtracting Source 3 increments, 12 of 14 forest-type samples have remaining TEQs less than 4 ng TEQ/kg, comparable to or lower than the TEQs for forest-type samples in the Washington statewide survey (Rogowski et al. 1999). The two higher remaining TEQs (8.96 and 23.6 ng TEQ/kg) are dominated by Source 2 contributions and are located near a major roadway and a landfill with heavy equipment operations.
- Source 3 has only minor contributions to two roadside-type samples collected outside of heavily developed areas of Port Angeles.
- Source 3 has large contributions to many of the upslope transect-type samples (57% to 81% for 6 of 9 samples), although Source 3 increments and total TEQs are low. This result was not anticipated as part of the Conceptual Site Model.
- Source 3 has the largest influence on the number of sample locations exceeding 11 ng TEQ/kg. Of the 40 samples out of 85 total locations that have total TEQs above 11 ng TEQ/kg, the number remaining if individual source increments are omitted is 25 without Source 1, 27 without Source 2, and only 12 without Source 3.
- Among the 15 samples with the highest total TEQ results (greater than 20 ng TEQ/kg), Source 1 alone contributes approximately 50% or more of total TEQ and more than 11 ng TEQ/kg to nine locations. Source 1 thus has the major influence on a subset of the samples with highest total TEQ results.

Source increment spatial pattern summary. The approach and conclusions for the evaluation of spatial patterns for the source increments determined by unmixing analyses are summarized as follows:

- Two-dimensional spatial mapping of soil total TEQ results was refined using source increment results from unmixing analyses.
- Concentration maps ("dot maps") for all samples coded by sample type were prepared for each of three separate source increment datasets, to evaluate patterns related to specific source profiles. A contour plot (using the Nearest Neighbor contouring technique) was also developed for Source 3 TEQ increments to further illustrate spatial patterns for those source increments.
- Source 1 increments show widely distributed, isolated "hot spots," consistent with property-specific dioxin/furan sources (e.g., tire burning or possibly chemical application of the herbicide 2,4,5-T), with most values (43 of 60 grid locations, or 72%) less than 3 ng TEQ/kg. Source 1 increments at all forest, road, and upslope sampling locations are small.
- Source 2 increments show a relatively even spatial distribution with many low concentrations (47 of 60 grid locations, or 78%, less than 5 ng TEQ/kg) and a small number of higher outlier values up to 9.7 ng TEQ/kg. Of all road, forest, and upslope sampling locations, only two forest sampling locations have higher outlier values for Source 2 increments.
- In contrast to Sources 1 and 2, Source 3 increments show strong spatial patterning with clusters of high values close to the former Rayonier Mill HFB stack, with 26 of 60 (43%) grid locations greater than 5 ng TEQ/kg and 10 of 60 (17%) greater than 10 ng TEQ/kg. Road and upslope Source 3 increments are small; forest sampling locations have comparatively elevated Source 3 increments, with 6 of 14 locations above 10 ng TEQ/kg.
- One cluster southeast of the former Rayonier Mill HFB stack (in the Gale's Addition area) is proximate to and generally downwind of the HFB location.
- A second cluster southwest of the former Rayonier Mill HFB stack is proximate to the HFB location, but not in a dominant downwind direction according to the wind roses from Ediz Hook. The representativeness of those off-site wind roses is uncertain. The spatial pattern and proximity of these elevated Source 3 increments to the southwest, as well as observations of Rayonier HFB stack plume behavior and the distance to other Port Angeles HFBs assumed to have similar Source 3 profiles, are factors to consider in evaluating any connection between this southwest cluster and the Rayonier HFB. A former medical waste incinerator co-located with the southwest cluster has no stack test data, but the TEQ profile for this type of source is not similar to the Source 3 profile.
- Beyond the proximate areas of higher Source 3 increments, values at grid sampling locations fall off substantially to the east and the south.
- Several higher Source 3 increments occur at the far western end of the soil dioxins/furans study area, closer to other potential HFB sources in Port Angeles. With available wind rose data, these additional higher Source 3 increment locations would be largely downwind of the other potential HFB sources and upwind of the Rayonier Mill.[3] As

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[3] The general terms upwind and downwind are used in this report to reflect the dominant annual wind directions as shown in available Port Angeles wind roses. These terms should not be misunderstood to be absolute or exclusionary: for example, locations denoted as upwind may nonetheless have been downwind for a comparatively

distances to the west from the former Rayonier mill increase, higher contributions from other HFBs are more likely.

- Source 3 increments contribute more than 40% to total TEQ concentrations for 38 of 41 (93%) grid- and forest-type samples in the eastern sampling zones, and 17 of 33 (52%) in western sampling zones. Source 3 has the highest TEQ increment of the three sources for 34 of 41 samples in the east zones, and for 16 of 33 western samples.
- The inverse distance relationship from the Rayonier HFB location for Source 3 increments, with a Source 3 TEQ profile similar to emissions from HFBs burning salt-laden wood, provides evidence that those HFB stack emissions have impacted off-property soils. Source 3 increments generally decrease, but not to zero, as distance from the Rayonier HFB increases (both upwind and downwind). In addition to the Rayonier HFB, other Port Angeles sources with a similar TEQ profile may contribute to Source 3 TEQ increments as mapped.
- Urban-to-rural gradients in total TEQs, Source 2 increments, and Source 3 increments, but not Source 1 increments, are shown in distance versus TEQ concentrations for east-zone plus upslope samples.

Mass balance evaluation summary. The approach and conclusions for the mass balance evaluations, based on Source 3 increments with a TEQ profile similar to emissions from HFBs burning salt-laden wood, are summarized as follows:

- Given the limited data available and the number of assumptions required to complete a Source 3 TEQ increments mass balance, the evaluations provided here are considered exploratory.
- Based on the results of unmixing chemometric analyses, Source 3 increments were estimated for each sample.
- The total mass of Source 3–related TEQ in sampled soils (0- to 3-inch depth interval over the entire study area) was calculated using a stratified (sampling zones) calculation approach. Using 70 of the 85 samples in this study, the calculated mass is approximately 7.5 grams TEQ.
- Accounting for the fact that only a small fraction of air-emitted dioxins are deposited locally (Lohman and Seigneur 2001), the calculated Source 3 TEQ mass in soils indicates cumulative source emissions (from one or multiple physical sources) on the order of tens of grams TEQ.
- Using current toxicity equivalency factors (TEFs), the only available Rayonier HFB stack test (in 1995) results in an estimated annual TEQ mass emissions rate of 0.077 grams TEQ/year.
- Dioxin emissions were almost certainly higher in the early decades of the 67 years of operations at the Rayonier Mill, although no measurements of early emissions are

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small fraction of an annual period, as reflected in a wind rose, and therefore would not be constantly or universally upwind.

available. The 16-fold reduction in HFB particulate emissions that was reported after upgrading of pollution control systems supports a conclusion that dioxin emissions over much of Rayonier's operating history were higher than those measured in 1995.

- Rayonier's HFB stack appears to be a credible source for cumulative dioxin emissions on the order of tens of grams TEQ.
- A 2009 stack test at the Nippon mill, when non-salt-laden wood was being burned in the HFB, resulted in estimated annual emissions of 0.0033 grams TEQ/year. Compared to the annual emissions estimate from the 1995 Rayonier HFB stack test, where salt-laden wood was being burned, this supports the conclusion cited in the literature that burning salt-laden wood can substantially increase dioxin emissions.
- Other large wood-products industry facilities that have operated in Port Angeles are likely to have also burned salt-laden wood wastes in HFBs, although no data are available to characterize dioxin emissions resulting from such practices at those locations. The dioxin TEQ profiles from multiple locations burning salt-laden wood wastes in HFBs are likely to be similar. Based solely on narrative operating histories and the scale of these other plants, their combined (and in some cases individual) cumulative over time dioxin emissions may well have totaled tens of grams TEQ, similar to the estimates for the former Rayonier Mill HFB.
- Other facilities with potentially significant cumulative HFB dioxin emissions are located several miles west of the former Rayonier Mill, generally upwind of areas sampled in this study. The largest impacts from those HFB emissions in the study area for this report are expected within the western portion of the study area; several locations with elevated Source 3 TEQ increments occur within the westernmost sampling zone W3. Rapidly decreasing, but non-zero, contributions from the upwind HFBs may extend farther eastward throughout the study area.
- The calculated soil mass for Source 3 increments restricted to only the east sampling zones (E1, E2, and E4) is 4.5 grams TEQ, which still indicates cumulative source emissions on the order of tens of grams. The distance from the upwind HFBs to the eastern sampling zones is considered sufficient to limit their contributions to small increments. This restricted soil mass calculation therefore suggests one or more sources with Source 3 TEQ profiles and emissions on the order of tens of grams located within rather than upwind of the study area.
- Residential wood burning may have a TEQ profile similar to Source 3 from the unmixing analysis. Contributions to mapped Source 3 increments from residential wood burning are expected to be spatially homogeneous and limited in magnitude. The estimated total amount of wood burned by residents annually, the fact that it is largely non-salt-laden wood, and the data from other urban soil dioxin studies all support a conclusion of relatively small magnitude impacts from residential wood burning.
- A former medical waste incinerator operated for approximately 15 years at the Olympic Medical Center, located close to the former Rayonier Mill. No stack test data are available for that facility. Based on stack test results for dioxins at two other Washington State medical waste incinerators, the Olympic Medical Center incinerator is not a credible source for cumulative dioxin emissions of tens of grams TEQ. Even absent a

facility-specific stack test for the former Port Angeles incinerator, information on TEQ profiles for this class of sources makes it highly unlikely that it is a significant source for the Source 3 increments in soil.

- The mass balance analysis considers possible contributions from several sources. Sources that could have contributed to the Source 3 TEQs in surface samples throughout the study area include the former Rayonier Mill HFB, several other HFBs located west (upwind) of the study area, and possibly residential wood burning throughout Port Angeles. Air emissions from residential wood burning are estimated to have had at most relatively small magnitude, spatially homogeneous contributions. Upwind HFBs that burned salt-laden wood, or that continue to burn non-salt-laden wood, are expected to have their greatest contributions to the study area for this report within the western portion of the study area, with decreasing contributions extending eastward throughout the study area. The former Rayonier Mill HFB is the primary Source 3-type source located within the study area and is centrally located with respect to many of the higher Source 3 increment soil concentrations. The upwind HFBs and the former Rayonier Mill HFB may have had comparable cumulative TEQ emissions, each at the appropriate order of magnitude to account for the mass of Source 3 increments measured in study area soils. Accurate quantitative estimates of source emissions are not possible because adequate facility-specific monitoring data are lacking.

Detailed evaluations of the soil dioxin/furan data collected in this study establish several key findings. Total TEQ concentrations in Port Angeles soils are higher than in other available studies of urban soils. Unmixing analyses produce one source profile (Source 3) similar to emissions from HFBs burning salt-laden wood. The source increments (source-related contributions to total TEQ) from that modeled source profile account for the higher total TEQs in Port Angeles; subtracting them from total TEQs, the remaining TEQs are similar to those in other urban studies. The spatial pattern of source increments for grid-type samples from that modeled source shows a strong inverse distance relationship in relation to the Rayonier HFB stack, with several outlying elevated source increments at the far western end of the study area. Exploratory mass balance analyses suggest that the former Rayonier Mill HFB and several other HFBs located west (upwind) of the study area may each have had cumulative TEQ emissions consistent with the required source emissions inferred from Source 3 increments mapping; the locations of these HFBs with respect to the study area influence their likely patterns of impacts.

Based on these evaluations, the major conclusion of this study is that dioxin/furan emissions from the former Rayonier Mill HFB stack have contributed to an elevation in TEQs in off-property soils in and near Port Angeles.

ES-6 Summary

The goal of this study was to increase understanding of dioxin/furan soil contamination in areas surrounding the former Rayonier Mill. The study’s specific objectives were to (1) determine the magnitude of dioxin/furan contamination in off-property surface soils potentially impacted by airborne emissions from the former Rayonier Mill, and (2) determine the contribution to measured soil dioxin/furan concentrations from the former Rayonier Mill emissions relative to contributions from other potential sources. A chemometric evaluation was used to separate the data into source-related increments. The data were evaluated through four lines of evidence (magnitude, spatial patterns, chemical patterns, and mass balance) to meet the objectives.

The magnitude of dioxin and furan concentrations sampled in Port Angeles ranged from 0.80 to 76.3 ng TEQ/kg; total TEQ values in this study are shifted higher than values from available comparable urban datasets. The chemometric evaluation identified three source patterns that account for the data collected. The concentrations of dioxin and furan congeners measured in Port Angeles soils reveal one pattern that is distinct for emissions from HFBs burning salt-laden wood. No other potential source profile was identified in the scientific literature that matches this pattern. The contributions to soil TEQs from the profile matching burning salt-laden wood account for the higher total TEQs found in Port Angeles in this study. Those contributions also have a distinct, clustered spatial pattern, in contrast to the patterns for contributions of the other two sources from chemometric analyses.. This spatial pattern, revealed by mapping the contributions of the HFB-type source, centers on the approximate location of the former Rayonier Mill HFB, with several outlying elevated source increments at the far western end of the study area.

The results of this study provide evidence that the emissions from the former Rayonier Mill HFB impacted the level of dioxin and furan concentrations in soil beyond the Rayonier Mill property boundaries. Further evaluations will be needed to define the extent of areal and vertical impact, to define background levels of dioxins and furans in Port Angeles, and to determine whether any cleanup actions will be needed.

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1.0 Introduction

The Washington State Department of Ecology (Ecology) initiated the Rayonier Mill Off-Property Soil Dioxin Study to increase understanding of polychlorinated dibenzo-*p*-dioxin (dioxin) and polychlorinated dibenzofuran (furan) soil contamination in areas surrounding the former Rayonier Mill. Dioxins and furans were emitted from the former Port Angeles Rayonier Mill during decades of pulp and paper production and potentially deposited on off-property soils in and near Port Angeles, Washington. “Off-property” refers to areas outside the former Rayonier Mill property boundary.

Ecology contracted with Ecology and Environment Inc. (E & E) to conduct the soil study. E & E managed the study, which involved collaboration of several consultants with diverse areas of expertise. Overall study design and data analysis were completed by independent consultant Greg Glass in coordination with E & E. All chemometric analyses were conducted by Infometrix Inc. In addition, Herrera Environmental Consultants Inc. (HEC) provided support for field sample collection and GIS database management. Laboratory analyses were performed by Axys Analytical Services Ltd. of Sidney, British Columbia, and Analytical Resources Inc. of Tukwila, Washington. Data validation was performed by EcoChem Inc. of Seattle, Washington. Additional resources and guidance critical to the study also were provided by representatives of the Lower Elwha Klallam Tribe (LEKT), City of Port Angeles, and Washington Department of Health, as well as by Ecology.

This *Rayonier Mill Off-Property Soil Dioxin Study Final Project Report, Public Review Draft* documents the culmination of the study. The report presents a summary of the study design, sampling and analysis protocol, and analytical results and an in-depth discussion of the data evaluation process, results, and conclusions. Previous documents produced for this study are listed and described below:

- *Rayonier Mill Off-Property Soil Dioxin Study Conceptual Site Model* (E & E 2008a) – Provides background information on dioxins and furans, including factors influencing their production, distribution, and fate in the environment and concentrations in soil over time; a description of the Port Angeles environment; a summary of existing dioxin and furan data collected in Port Angeles and other locations in Washington state; and a description of known and potential sources of dioxins and furans in Port Angeles.
- *Rayonier Mill Off-Property Soil Dioxin Study Soil Sampling Plan and Responsiveness Summary* (E & E 2008b) – Provides a detailed description of the objectives for this study; the process for defining the boundary for the study area (hereafter called the “soil dioxin study area”) based on existing air modeling and monitoring data and land features; methods for distributing samples throughout the soil dioxins/furans study area and determining sample density and sample depth; selected analytes and analytical methods; and a brief introduction to sample collection procedures, data evaluation, and reporting.
- *Rayonier Mill Off-Property Soil Dioxin Study Sampling and Quality Assurance Plan* (E & E 2008c) – Provides methods for selecting properties and contacting property owners to request permission to collect samples; sample collection procedures, including selection of the sampling location, sampling equipment and methods, decontamination

procedures, labeling, and sample documentation; cultural resources monitoring during sample collection; health and safety practices; laboratory methods; quality assurance and quality control procedures; and data validation procedures.

- *Rayonier Mill Off-Property Soil Dioxin Study Data Summary Technical Memorandum* (E & E 2009) – Provides a general overview of the samples collected for the study, data analysis and validation methods, and data management methods. The memorandum also provides the complete dataset provided by the validation firm, EcoChem; the final working database following data reduction; summary statistics for the sample results; and various visual presentations of the data, including sample location maps, maps showing dioxin/furan concentrations, profiles of congener contributions to sample TEQs [see definitions for congener and TEQ below], scatter plots, and location and concentration data by direction and distance from the former Rayonier Mill.

1.1 Overview of Dioxins/Furans

Dioxins and furans are two classes of chemicals that are structurally similar in that they both contain two carbon ring structures. All dioxins include two oxygen atoms, while all furans include one oxygen atom, as shown in Figure 1-1. There are 210 unique dioxin/furan compounds, each called a "congener" (75 dioxin and 135 furan congeners), which differ from each other in the number and position of chlorine atoms on the carbon rings.

Dioxin/furan congeners contain one to eight chlorine atoms, resulting in eight families, or homolog groups, ranging from those containing one chlorine atom, monochlorodibenzo-*p*-dioxins (MCDDs) and monochlorodibenzofurans (MCDFs), to those containing eight, octachlorodibenzo-*p*-dioxins (OCDDs) and octachlorodibenzofurans (OCDFs). Figure 1-1 shows each numbered carbon atom, corresponding to possible positions for the chlorine atoms.

Although there are 210 unique dioxin/furan congeners, only 17 of these are typically evaluated because they are considered by the U.S. Environmental Protection Agency (EPA) and the World Health Organization to be the most toxic. These 17 congeners have chlorine atoms in the 2, 3, 7, and 8 positions shown in Figure 1-1. In this study, the terms "dioxins" and "furans" will be used to refer to the 17 congeners of primary interest, listed in Table 1-1. This report also will refer to these 17 congeners as the "2,3,7,8-substituted congeners" because chlorine has been substituted for hydrogen at the 2, 3, 7, and 8 positions.

Concentrations of the 17 dioxins/furans of primary interest are often expressed as a total toxic equivalent concentration (TEQ) to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD). This means that the concentrations of the other 16 congeners have been adjusted based on a toxicity equivalency factor (TEF) that scales each congener's potency relative to 2,3,7,8-TCDD. The concentrations are presented as mass of chemical per mass of soil, such as 1.5 nanograms of 2,3,7,8-TCDD TEQ per kilogram of soil (1.5 ng TEQ/kg). The TEFs assigned to each congener are consistent with Ecology guidance (2007; Van den Berg et al. 2006) and are presented in Section 6. The most potent congeners, 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD, are assigned a TEF of 1, while the least potent, OCDD and OCDF, have the smallest TEF, 0.0003.

Federal and state environmental regulatory and health agencies are interested in dioxins/furans because they are toxic to humans and wildlife. Once released into the environment, dioxins/furans resist biodegradation, do not dissolve in water, and attach strongly to particles such as soil, dust, and sediment. This means that they are persistent and can bioaccumulate in people and animals and can be measured in environmental media long after they have been released. Despite their persistence and ubiquitous presence, levels of dioxins/furans in the environment have been declining since the 1970s due to improvements in air pollution control technologies for combustion and incineration facilities and cleanup of dioxin-contaminated areas (EPA 2003).

Dioxins/furans enter the environment from a variety of sources. Except for small quantities used in research, neither compound is created intentionally. Instead, dioxins/furans are unwanted by-products of chemical manufacturing and combustion or incineration processes involving chlorine compounds. For example, dioxins are most notorious for their presence as a contaminant in the herbicide 2,4,5-T and in Agent Orange. They can also be produced during incineration of wood, oil, and wastes. Major contributors of dioxins/furans to the environment include:

- Incineration of municipal solid waste and medical waste
- Secondary copper smelting
- Forest fires
- Land application of sewage sludge
- Cement kilns
- Coal-fired power plants
- Residential wood burning
- Chlorine bleaching of wood pulp
- Backyard burning of household waste
- Byproducts and derivatives of chemical production (e.g., pentachlorophenol; PCBs; 2,4,5-T)
- Hog fuel boilers (HFBs) burning salt-laden wood

Dioxins/furans are present at some level throughout the environment, in air, food, water, soils, and sediments. Dioxins/furans tend to be found in higher concentrations near industrial areas but are present in various concentrations throughout urban and rural areas and even in remote wilderness regions. Urban soil concentrations of dioxins/furans commonly represent the combined influences of multiple sources.

1.2 Former Rayonier Mill History and Description

The Olympic Forest Products Company constructed a pulp mill along the waterfront in 1930. The mill later merged with two independent companies in 1937 to become Rayonier Inc. In 1968, International Telephone and Telegraph (ITT) Corporation purchased Rayonier Inc., renaming the mill ITT Rayonier. The mill operated under ITT Corporation until 1994, when the mill was spun off from ITT Corporation and resumed operating under the name Rayonier Inc. until its closure in 1997. Site dismantling was completed in 1999, although a few structures still remain on the property. Descriptions of mill history and operations are provided by Foster Wheeler Environmental Corporation (FWEC 1997) and Integral Consulting Inc. (2006).

The Rayonier property, which has been almost completely cleared of its mill facility and outbuildings, totals 80 acres. The property is in Section 11 of Township 30 north, Range 6 west, at a latitude of 48° 07’ 00” north and longitude of 123° 24’ 25” west. Most of the property extends into the eastern portion of Port Angeles Harbor. The northern portion of the property is flat, with steep bluffs rising rapidly to approximately 75 feet above National Geodetic Vertical Datum (NGVD) immediately to the southeast and southwest (HLA 1993). The terrain continues to rise to approximately 200, 265, and 150 feet above NGVD within approximately 1 mile southeast, south, and southwest of the property, respectively.

Rayonier used wood chips, including salt-laden wood, in the on-site HFB (Integral 2006). Due to the location of the mill on Port Angeles Harbor and the abundance of wood as a source of fuel for onsite burners, the mill burned wood chips and wood wastes coming from logs floated in Port Angeles Harbor. Using salt-laden wood in HFBs can result in significantly higher emissions of dioxins/furans than can burning salt-free wood (Duo and Leclerc 2004, Lavric et al. 2004, Luthe et al. 1997b, Luthe et al. 1998a, Pandompatam et al. 1997, Preto et al. 2005, Uloth et al. 2005). Combustion of salt-laden hog fuels in the HFB is considered the primary source of dioxins/furans emitted from the former Rayonier Mill. Dewatered sludges from the mill’s wastewater treatment system were also burned in the HFB.

In addition, chlorine dioxide was used to treat pulp in the bleach plant. After bleaching, the pulp was transported to dryer machines. The dryer machines rolled and dried the pulp, producing rolls of pulp sheets. Dioxins/furans may have been created during the drying process if drying temperatures were sufficiently high.

The former Rayonier Mill went through various regulatory and structural changes over the history of its operations. Under normal operating conditions, air emissions were released from numerous sources on site, including the recovery and HFB stacks, the chlorine dioxide generator, and vents in the bleach plant, acid plant, and blowpits. The recovery boiler was constructed in 1974, in part to reduce sulfur dioxide emissions. At the same time, scrubbers and demisters were placed on the recovery boiler stack. A scrubber and demisters also were installed on the HFB stack in 1974 (FWEC 1997).

Limited testing performed in 1988 confirmed the presence of dioxins/furans in samples collected from the HFB at the former Rayonier Mill, including bag house ash (1,310 ng TEQ/kg) and washed ash (170 ng TEQ/kg; FWEC 1997). Samples collected from the HFB in 1989 contained total dioxin and total furan concentrations of 2,700 ng/kg and 19,000 ng/kg in boiler ash and 22,000 ng/kg and 22,000 ng/kg in filter ash, respectively (FWEC 1997). Additional samples of bag house fly ash (total TCDD 160,000 ng/kg; total TCDF 64,000 ng/kg) and filter ash (total TCDD 380,000 ng/kg and total TCDF 33,000 ng/kg) were collected in 1991 and 1993, respectively.

In 1995, stack tests of air emissions from the former Rayonier Mill HFB confirmed the presence of dioxins/furans (FWEC 1997). A single source test performed in 1995 yielded a load of 0.17 milligrams (mg) TEQ/day (FWEC 1997; note that this calculation used an earlier set of TEFs). In 1996, concentrations of 2,3,7,8-TCDD (110 ng/kg) and 2,3,7,8-TCDF (350 ng/kg) were detected in vacuum filter ash (FWEC 1997). Generally, dioxin/furan loading is associated with fly ash as opposed to grate or filter ash (Yake et al 1998). A complete description of these sample results is provided by FWEC (1997) and Integral Consulting Inc. (2006).

2.0 Study Objectives

The former Rayonier Mill property has been designated as a site for cleanup actions under Washington's Model Toxics Control Act (MTCA). Ecology has not yet determined if the site should be extended to include off-property areas within greater Port Angeles that have been impacted by mill emissions.

The goal of the Rayonier Mill Off-Property Soil Dioxin Study is to increase understanding of dioxin/furan soil contamination in areas surrounding the former Rayonier Mill, including the magnitude and likely sources of contamination of surface soils. Specific study objectives include:

- Determine the magnitude of dioxin/furan contamination in off-property surface soils potentially impacted by airborne emissions from the former Rayonier Mill, and
- Determine the relative contribution[4] to measured soil dioxin/furan concentrations of former Rayonier Mill emissions compared with other potential sources.

While this study assesses the impacts from cumulative mill emissions, other sources of dioxins/furans in soils are recognized. These include, among others, diffuse urban plume sources, combustion process emissions from multiple Port Angeles facilities, and the introduction of dioxins/furans from various types of chemical applications or spills to soils . The study design attempted to account for these other sources while meeting the objectives listed above. The patterns of soil contamination surrounding a single, isolated air emissions source are expected to be different in predictable ways if evaluated over a relatively large area, with concentrations decreasing gradually as distance from the source increases; that is, an observable gradient is expected. However, these patterns may be largely obscured if multiple sources are present. Moreover, experience has shown that at small, local spatial scales, the variability in soil contaminant concentrations among nearby sampling locations can be quite large, especially in more developed land use areas.

Characterization of the upper range of soil dioxin/furan concentrations throughout the soil dioxins/furans study area was attempted wherever feasible, as a means of confirming whether and to what degree impacts from Rayonier Mill emissions exist on local soils. Of all of the dioxin/furan sources associated with former Rayonier Mill operations, only the air emissions pathway associated with mill operations was of interest for this study. Direct disposal of mill-related materials (e.g., ash and wastes) was excluded from the scope of this study[5].

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[4] In evaluating the relative contribution of former Rayonier Mill emissions versus other sources, it is not the objective of this study to perform detailed quantitative allocations among potential sources or to apportion liability or responsibilities among potentially liable parties. The former Rayonier Mill is recognized as being one of several locations in Port Angeles that historically burned salt-laden wood.

[5] Area landfills where dioxin-containing ash from the former Rayonier Mill was disposed are the subject of other investigations and monitoring programs.

2.1 Magnitude of Contamination

The first objective of the study was to better define the total soil dioxin/furan concentrations in areas potentially affected by airborne emissions from the former Rayonier Mill. The study aimed to characterize the magnitude of dioxin/furan contamination in surface soil, including the upper-range concentrations of dioxins/furans throughout the soil dioxins/furans study area. Existing soil studies demonstrate a relationship between concentration and distance from the source; the trend is for dioxin/furan levels to be greatest near a specific emission source and to decrease as distance from the source increases (EPA 2003), in spite of localized variability.

Even in the absence of a dominant source of dioxin/furan emissions, levels of dioxins/furans tend to be greater in urban settings and to decrease with distance from urban areas. This is referred to as the “urban plume” effect (EPA 2003). In fact, dioxins/furans have been detected at measurable concentrations even at remote locations. Their ubiquitous distribution is the result of long-range atmospheric transport.

As discussed in the Conceptual Site Model (CSM; E & E 2008a), concentrations in soil may be influenced by meteorological conditions during the operating or emission period; the presence or absence of ground cover that scrubs dioxins/furans from air; ground surface slope and erosion of soils containing dioxins/furans; soil disturbances such as landscaping, filling, or application of amendments; and the chemical characteristics of soil, such as organic carbon content.

To accomplish the objective of determining soil dioxin/furan concentrations in off-property upland soils, samples were collected over a relatively large spatial area surrounding the former mill. Consistent with the conceptual model of spatial patterns around a point source of air emissions, sampling densities were greater in areas closer to the former mill where both local variability and upper-range concentrations were expected to be higher. Sampling densities were lower in more distant areas where the range in variability was expected to be less.

More samples were collected near the source to increase the probability of capturing the upper range of dioxin/furan concentrations. Characterization of the upper range of concentrations was particularly important to provide information on the maximum impact of former mill emissions. In addition, this provided the most useful information to distinguish between urban plume and mill impacts, in terms of dioxin/furan concentrations and congener profiles. These distinctions are crucial to meeting the second objective, source identification.

Although the number of locations sampled in this study is large compared with most other studies of dioxins/furans in soil, the inherent variability of dioxin/furan concentrations in highly developed urban area soils makes it difficult to delineate the complete spatial pattern for dioxins/furans. The focus on the upper range of dioxin/furan levels in this study design reflects this problem and supports the first study objective, determining whether there are impacts that can be associated with former mill emissions, but does not necessarily support determining the full spatial footprint of such impacts.

2.2 Source Identification

The second objective of this study was to evaluate the dioxin/furan results with respect to source identification and source contributions. The former Rayonier Mill was located near other recognized dioxin/furan sources. Therefore, the approach to source identification addresses co-mingling of dioxins/furans from potentially different sources.

Other potential dioxin/furan sources in Port Angeles, apart from the Rayonier Mill, were reviewed and summarized during the development of the study design (E & E 2008b). The locations of the more notable point sources are shown in Figure 2-1. Historically Port Angeles was a center of major wood-products industries (Martin 1983, Plywood Pioneers Association 2001, Sanborn Fire Insurance Maps 1897-1964), several of which received materials at log ponds in Port Angeles Harbor, which led to burning salt-laden bark and wood wastes in HFBs. Three such facilities—Nippon Paper (formerly Daishowa and Crown Zellerbach), K Ply (formerly PenPly), and Fibreboard (formerly Crescent Boxboard), all of which were large—are shown in Figure 2-1. Several historical shoreline sawmills may also have burned salt-laden wood waste in HFBs. The Merrill & Ring sawmill shown near the Nippon mill,at the base of Ediz Hook was also the location of several earlier sawmills (Sanborn Fire Insurance maps). Numerous early-period smaller-scale operations of diverse types are noted on the Sanborn Fire Insurance maps as having been fueled by wood or [wood] refuse. Those facilities included sawmills, shake and shingle mills, salmon and clam canneries, an early electric light works, a brewery, a steam laundry, and a cooperage company.

Other point sources in Figure 2-1 include a former medical waste incinerator at Olympic Memorial Hospital, two crematoria, and several larger boilers. Dioxin/furan source test results for these other potential point sources in Port Angeles are almost entirely lacking. Numerous other typical urban sources of dioxins/furans are assumed to contribute to some degree to Port Angeles soils. Such typical sources include vehicle emissions, residential wood burning, backyard burning (burn barrels), structural fires, and applications of dioxin-containing chemical products.

Emissions from different dioxin/furan sources have been characterized by the chemical profile or chemical “fingerprint” of the 2,3,7,8-substituted congeners (EPA 2003a, Cleverly et al. 1997, Pandompatam et al. 1997). The amount of each dioxin/furan congener formed varies depending on the source, resulting in a distinguishable pattern, or chemical fingerprint, characteristic of the source. Biogeochemical processes such as weathering may alter these patterns, so the statistical significance of differences found between source materials may decrease with increasing time since deposition. Multiple sources of the same or very similar type (e.g., multiple cement kilns, or multiple HFBs all burning salt-laden wood) may have very similar chemical patterns for dioxin/furan emissions. In such cases, factors other than chemical patterns—for example, spatial patterns—are also important for evaluating source contributions.

A review of the literature and discussions with the project chemometrics expert (Ramos 2008) indicate that collecting samples from an area within which the chemical profiles for dioxins/furans are expected to vary as a result of contributions from various sources may help identify different sources and support source contribution evaluations. This factor was considered in selecting the soil dioxins/furans study area boundaries.

To meet the source identification and source contribution objective of the study, soil samples were analyzed for the 17 2,3,7,8-substituted dioxin/furan congeners. The chemical patterns within this dataset were evaluated using several statistical techniques, as described in Sections 7 and 8, to identify a set of source patterns contributing to soil contamination over the entire soil dioxins/furans study area and to estimate the contribution of each such source pattern to each sampling location. The modeled source contributions to TEQ were used in further evaluations of spatial patterns and mass emissions related to individual source profiles.

2.3 Issues Outside the Scope of This Study

The objectives of this study were to evaluate concentrations and spatial patterns for dioxins/furans in soil and reach a conclusion on the occurrence of off-property impacts, if any, from Rayonier Mill emissions. The objectives did not include the following:

- Delineation of the entire extent, or boundary, of contamination resulting from emissions from the former mill;
- Complete characterization of contamination at sampled properties to support exposure and risk assessments or cleanup actions;
- Definition of background soil dioxin/furan levels; or
- Interpolation of results from sampled to not-sampled properties.

This study focuses on identifying the upper range of dioxin/furan concentrations within the predominant impact area of former mill emissions. Delineation of the full extent of emissions was outside the scope of the study, as it would have required in-depth investigation to determine appropriate background levels of dioxins/furans in addition to the full horizontal and vertical extent of contamination.

Due to local variability, the dioxin/furan concentrations measured in this study may underestimate the true maximum concentrations present on an individual property or in any local subarea. Also, the sampling performed at each sample location was limited to one portion of the property and did not include a full characterization of the horizontal extent of the entire property. This study also did not include characterization of chemicals at multiple soil depths to determine the vertical extent of contamination. For these reasons, the data generated for this study alone are not sufficient for characterizing properties to support cleanup actions.

Localized variability also prevents effective interpolation of dioxin/furan concentrations from sampled to unsampled properties. While it may be possible to generalize about dioxin/furan concentration ranges in soils for various locations across the soil dioxins/furans study area, it is not reasonable to attempt to predict soil concentrations on a property-specific basis. Factors affecting soil concentrations at the individual sample location or property-specific level are discussed in the CSM (E & E 2008a).

In addition, undisturbed areas are ideal soil sampling locations for this study, as they are most likely to represent deposition from former mill air emissions that has not been diluted due to earth-moving or erosion. Samples collected at developed (residential) properties focused on least-disturbed soils, rather than seeking to fully characterize dioxin/furan concentrations over the entire parcel or areas where people are most likely to contact soil (garden soils, ornamental planting strips, play areas, soils lacking vegetative cover). The limited sampling locations per property in this study is not well suited to completing exposure and risk analyses, which require more intensive sampling of each property.

While the current study does not fully address questions related to defining background concentrations, delineating the full extent and exact boundaries of mill impacts, or evaluating potential exposures and human health risks, it does provide some information related to each of those issues. That preliminary information can be used to focus additional studies so they can be performed cost-effectively.

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3.0 Study Design

The rationale for the study design is described in detail in the soil sampling plan (SSP; E & E 2008b). This section presents a summary of the study boundary definition and a brief explanation of how samples were allocated within the soil dioxins/furans study area.

3.1 Definition of Study Boundary

The soil dioxins/furans study area boundary was selected considering the following factors:

- Review of historical studies conducted in Port Angeles, including odor and air modeling studies;
- Inclusion of areas near other potential sources in the vicinity of the former Rayonier Mill;
- Inclusion of preferred land cover areas; and
- Maintenance of adequate sampling density.

A complete discussion of these factors and their contribution to defining the soil dioxins/furans study area is provided in the SSP (E & E 2008b). The selected soil dioxins/furans study area surrounds the former mill, extending to Tumwater Creek on the west, to Buchanan Drive on the east, and to Lauridsen Boulevard on the west side of the southern border (Figure 3-1). The east side of the southern border extends approximately 1 mile inland from the bluff to include the Drennan-Ford Funeral Home and Crematory. The entire soil dioxins/furans study area encompasses approximately 4.2 square miles.

A review of the literature on studies of dioxin/furan air emissions sources indicates that the maximum distance at which soil impacts have been observed along gradients from a source is approximately 2 to 3 miles. The area defined for this study is consistent with those distances, extending approximately 3 miles east (downwind) of the former Rayonier Mill and approximately 2 miles west (upwind); see Figures 2-1 and 3-1.[6] The majority of emitted dioxins/furans are believed to be transported away from the source rather than being deposited in the immediate vicinity of the source (Lohman and Seigneur 2001).

A primary factor affecting transport of air emissions from the former Rayonier Mill site is the annual wind rose. A wind rose for 2006 from the Olympic Region Clean Air Agency's station at the base of Ediz Hook, to the west of the former Rayonier Mill site, is provided in Figure 3-2. Prevailing winds in this 2006 wind rose are from the west and west-southwest, indicating that primary upland impacts from Rayonier emissions would be to the east. A similar annual wind rose at this same station from 2001 has prevailing winds from the west and west-northwest (see Integral Consulting 2006, Appendix H), indicating dominant impacts to the east and east-southeast. The 2001 wind rose was used for a previous deposition modeling study (Integral Consulting 2006, Appendix H). In addition to year-to-year variations in the wind rose for the

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[6] The general terms upwind and downwind are used in this report to reflect the dominant annual wind directions as shown in available Port Angeles wind roses. These terms should not be misunderstood to be absolute or exclusionary: for example, locations denoted as upwind may nonetheless have been downwind for a comparatively small fraction of an annual period, as reflected in a wind rose, and therefore would not be constantly or universally upwind.

Ediz Hook station, its distance from the former Rayonier Mill site may make it less than ideally representative of conditions at the Rayonier location. Wind directions near the Rayonier site were observed to be more variable under conditions of light wind speeds, and numerous instances of non-linear plume behavior and nearshore fumigation were seen (Werner 2010). Wind data also were collected at the former Rayonier Mill site (but did not have independent data validation). Wind roses for 1983 to 1989 (see FWEC 1997) and 1998 (see Integral Consulting Inc. 2006) for the Rayonier Mill site show differences from the wind roses at Ediz Hook, with more frequent winds from southerly directions and somewhat more frequent winds from the east-northeast.

The soil dioxins/furans study area extends farther to the east than to the west, consistent with the annual wind rose pattern in which westerly wind directions dominate. The eastern extension of the soil dioxins/furans study area encounters less-developed lands that reflect the anticipated urban-to-rural gradient for urban plume impacts. Suitable forested properties also are more available for sampling within the extended eastern portion of the soil dioxins/furans study area.

A small number of samples also were allocated outside of the primary mapped soil dioxins/furans study area. These additional samples were collected along three north–south transects south of the soil dioxins/furans study area. These samples are at higher elevations and are more distant from the urbanized Port Angeles area and most local sources of dioxin/furan emissions.

As noted in the SSP (E & E 2008b), undisturbed, forested areas were preferred for sample collection but these areas are limited within the vicinity of the former mill and typically occur on steep slopes along the shoreline or in creek ravines. Because steep slopes and ravine bottoms are subject to erosion or additional soil deposition, they were excluded from the soil dioxins/furans study area.

3.2 Methods for Sample Location Selection

The following five steps led to selection of sample locations:

- Delineation of sampling zones
- Distribution of samples within zones
- Selection of within-grid sample locations
- Selection of within-property sample locations
- Selection of sampling depth interval

The soil dioxins/furans study area encompasses approximately 4.2 square miles. This area was divided into seven distinct sampling zones, shown in Figure 3-3. The primary purposes for delineating sampling zones were (1) to distinguish areas of different land use and land cover, and (2) to allow variable sampling densities in different portions of the soil dioxins/furans study area.

The zones were designated as west (W1, W2, W3) or east (E1, E2, E3, E4) with reference to the former Rayonier Mill site and Ennis Creek. Zones W1, W2, and W3 represent more densely developed, urban properties. Zones W1 and W2 encompass areas with a large number of odor complaint locations, as recorded during an odor study completed in the early 1990s while the mill was operational (TRC 1992). Zone W1 and the Highway 101 corridor are dominated by commercial properties, whereas Zones W2 and W3 consist of primarily residential properties.

Zones E1, E2, E3, and E4 represent less-developed areas, although with mostly disturbed soils. Of these four sampling zones, Zone E1 (Gales Addition) has the most residential land use. Zones E2, E3, and E4 are dominated by open fields, agricultural areas, and wooded lots. Zones E1 and E3 had a larger number of odor complaint locations than Zones E2 and E4 (TRC 1992).

In delineating sampling zones within the defined soil dioxins/furans study area, creeks and the steep side slopes along creek ravines were excluded because of the potential for erosion and flooding to affect the representativeness and interpretation of surficial soil measurements. Also, the relatively large Peninsula Golf Course within Zone E3 was developed fairly recently and is subject to fairly intensive maintenance, so that property was excluded.

After delineating the soil dioxins/furans study area and sampling zones, the next step in sample design was to allocate the 100 samples allowed for this study. A total of 21 samples were assigned to three types of targeted locations, leaving 79 samples to be allocated for broad coverage across all seven sampling zones. Figure 3-4 presents grid cells designated for each zone, which were used to obtain relatively even coverage within each zone. The proposed number of spatial coverage samples within each zone, plus additional targeted location sample counts, is summarized in Table 3-1. The actual number and distribution of collected samples is discussed in Section 4.

Since the dominant annual wind directions according to available wind roses are westerly, more samples were allocated to zones east versus west of the former mill. Relatively more samples (greater sampling densities) were allocated to areas closer to the former mill site. The conceptual model for an air emissions source, as well as information from the odor complaint and deposition modeling studies, indicates that the magnitude of impacts from mill emissions should decrease with greater distance downwind of the mill.

The 21 samples from targeted or preferred locations were proposed to meet three purposes:

- Ten samples were allocated for forested areas in Zones E2 and E4. Those samples were included to investigate the dioxin/furan gradient along the primary downwind direction from the mill in areas mostly likely to act as a reservoir for dioxins/furans emitted over time.
- Nine samples from three transects (three samples each) were targeted in upslope areas south of the main soil dioxins/furans study area, as shown in Figure 3-5. The transects were aligned north–south and reflected a gradient away from urban land use to more rural areas, in a non-prominent wind direction according to the area wind rose. These samples were intended to allow examination of a regional-scale pattern in magnitude and congener pattern for dioxins/furans.
- Two additional samples were allocated for high-traffic areas along Highway 101, in the less-urbanized eastern portion of the soil dioxins/furans study area, to characterize the potential source pattern and contribution of dioxins/furans from transportation sources.

Selection of candidate properties within the approximate sampling zone grid layout involved four considerations: (1) preference for forested (undisturbed) locations, (2) need to achieve spatial coverage across sampling zones, (3) collection of no more than 100 samples, and (4) need to obtain access agreements from property owners prior to sampling. After preferential selection of forested or undisturbed properties, properties with the longest history since development or disturbance were targeted.

Once the candidate properties for sampling were selected and the property owner provided access, the precise location for sample collection on the property was selected by the field sampling team. Exclusion and preference criteria, and observations and information obtained from occupants and owners, were applied to identify specific locations within properties for collecting soil samples. The general principle was to try to collect soils that were the most representative of long-term deposition and least disturbed locations within properties.

Small-scale composite samples, consisting of five subsamples each, were collected at each selected location to better represent typical values at the compositing spatial scale. The compositing approach is consistent with the protocols in other studies of soil dioxin/furan contamination (EPA 2007a, Rogowski et al. 1999), although details of the compositing strategy differ across studies.

Uppermost soil intervals are most representative of potential human contact with and exposure to soil contaminants, and, absent physical disturbance of the soils, these intervals typically contain the highest concentrations of air-deposited dioxins/furans at a sampling location. A number of dioxin soil studies have incorporated depth intervals ranging from 0–2 inches to 0–6 inches (Rogowski et al. 1999; EPA 2007a, 1992; Brzuzy and Hites 1995). A sampling depth interval of 0 to 3 inches was selected for this study to allow for adequate quantification of dioxins/furans in soil and reduce the possibility of dilution that may occur when obtaining a deeper interval.

3.3 Volunteer Recruitment

The sampling and quality assurance plan (SQAP; E & E 2008c) outlines the process for identification of properties targeted for recruitment. Targeted properties were those that appeared to be least disturbed and to best represent potential accumulation of dioxin/furan emissions deposition. Recruitment activities followed the process outlined in the SQAP but the activities followed a shortened schedule, with recruiting beginning in early August and continuing through the field sampling event in mid-September 2008.

During the candidate property identification process, aerial photos with a parcel boundary overlay were reviewed for the entire soil dioxins/furans study area to identify parcels that appeared to have the greatest coverage of forest or other type of vegetation. Candidate properties located within the City of Port Angeles then were cross-referenced with building age data obtained from Clallam County to eliminate those that had been developed after 1977 and all property locations were reviewed on topographic maps to eliminate those that were situated on steep slopes. In addition, records from the local fire departments were reviewed to eliminate properties with a reported fire occurrence.

Candidate properties then were assigned a tier level, with Tier 1 properties being the most ideal for sampling and Tier 3 being least ideal but acceptable if no other properties were available. Tier E properties were those that were excluded due to recent development, soil disturbance, or other confounding factors. Specifically, the tiers were:

- Tier 1 – Undeveloped property of at least 1 acre of open space or forest that appeared to be at least 30 years old.
- Tier 2 – Partially developed property (e.g., residential or commercial and open field) with improvements constructed prior to 1977 and forested area that appeared to be at least 30 years old or undeveloped property less than 1 acre.
- Tier 3 – Developed property (e.g., residential or commercial) with exposed soil or vegetative land cover and buildings constructed prior to 1977.
- Tier E – Excluded properties that have been developed or otherwise disturbed since 1977.

Once candidate properties were identified within each upslope transect area and grid cell for each zone, letters were sent via U.S. mail to the property owners requesting permission to collect soil samples. Three to five property owners in each grid cell and upslope transect area were contacted. In addition to mailing requests to property owners, study team members visited Port Angeles to conduct in-person recruiting over a two-week period in late August 2008.

Approximately 450 letters requesting permission to sample were mailed to residents in early August 2008. An additional 150 letters were left with residents during door-to-door recruiting. Of these 600 residents, approximately 150 returned signed access agreements, granting permission to collect a soil sample from their property. In addition, approximately 30 residents volunteered to participate in the study after hearing of the project through environmental groups, Ecology's website, public meetings, and word-of-mouth. Ultimately, 10 residents retracted their signed access agreements after hearing that the Port Angeles City Council initially voted against allowing Ecology to collect soil from city properties.

Residents who provided signed access agreements were interviewed to obtain additional information about their property. Properties were excluded if they had been developed or otherwise disturbed since 1977 or were otherwise not suitable for sampling, as defined by the exclusion criteria listed in the SQAP (E & E 2008c). Candidate properties also were visited by E & E staff prior to sampling to identify appropriate sampling locations. When more than one suitable candidate property was identified within a grid cell or upslope transect area, the property with the longest history since development or influence from non-mill dioxin/furan sources was selected as the sample location for a particular grid cell or targeted sample area.

In addition to private properties, city-, county-, and state-owned properties were considered for sampling. Ecology worked with the relevant agencies to obtain permission to sample public properties. Ultimately, permission was granted for access to properties owned by the state departments of Natural Resources, Fish and Wildlife, and Transportation.

A total of 78 properties were considered acceptable for sampling during the September 2008 field sampling event. Additional access agreements were obtained following the September 2008 field sampling event from private residents, Rayonier Inc., and the City of Port Angeles. Access was not granted by Clallam County. A second field mobilization was initiated in November 2008 to collect samples from an additional seven properties to which late access was granted, yielding a total of 85 sampled properties.

4.0 Soil Sampling Summary

Surface soil samples were collected by E & E and HEC staff September 3–17 and November 10–11, 2008, from seven gridded zones and three upslope transects. A total of 85 investigative samples were collected throughout the soil dioxins/furans study area, consisting of four sample types: grid (collected primarily from residential yards), forest, roadside, and upslope transect. A summary of sample types is provided in Table 4-1; sample locations for each zone and the upslope transect areas are shown in Figures 4-1 through 4-8.

The soil sample collection strategy is outlined in the SQAP (E & E 2008c) developed for this project. Portions of the SQAP are reiterated in this section along with deviations from the plan.

4.1 Sample Collection Methods

As mentioned in Section 3.2, each sample consisted of a composite of five subsamples. The sample locations were selected from the least-disturbed portion of each sampled property and each location was selected to represent a consistent set of depositional and land use conditions. The following features were excluded when selecting sampling locations within sampled properties:

- Disturbed areas at developed sites (e.g., construction sites, areas around concrete pads or foundations, telephone and electric poles, landscaping and ornamental planters, building drip lines, down spouts, gardens, dog runs, and areas of animal burrowing activity); soil was not collected within 6 feet of disturbed areas.
- Areas near wooden structures where treated wood may have been used; soil was not collected within a 20-foot radius of creosote-treated wood or within 6 feet from other forms of treated wood.
- High-traffic areas (e.g., parking lots, roadways, sidewalks); soil was not collected within 6 feet of these areas.
- Burn pits, fire pits, and areas adjacent to chimneys of wood-burning fireplaces; soil was not collected within 20 feet of these areas.
- Steeply sloped areas or areas potentially shielded from deposition of Rayonier Mill emissions.
- Hummocks, paths used by animals or humans, areas lacking ground cover, and other areas disturbed by treefall or animal digging within forested areas.
- Forested areas dominated by immature trees less than 30 years old, recently reforested areas, and areas with evidence of recent fires.
- The transitional area between forested and open/developed properties where dumping is more likely to occur.

The criteria for sample exclusion were used at all locations, including avoiding sample collection within 20 feet of any burn areas such as fire pits, burn pits, chimneys, and recent forest fires. Samples were not collected in several forested areas with charred stumps and fire-cracked rock deformed during forest fires. Despite attempts to avoid sampling in burn areas, charred wood was noted to be present at 23 of the 85 sampling locations, primarily (15 of 23 locations) in the eastern sampling zones (Table 4-2). The presence of charred wood in many instances may reflect post-logging slash burning prior to redevelopment of forest lands. In the majority of cases when charred wood was observed at a property being sampled, an attempt was made to move the soil sampling locations within that property to avoid charred wood in the collected sample. Only a small number of sample jars were observed to contain small pieces of charred wood (Table 4-2), although the possible inclusion of fragments too small to be observed cannot be discounted. Since wood burning is a recognized potential source for dioxins/furans, the possible presence of charred wood in a subset of samples was evaluated as a potential confounding factor for data evaluations. Nearly identical source profiles resulted from unmixing analyses of chemical patterns (see Section 8.3 for a discussion of unmixing analyses) regardless of whether the 23 samples from locations where charred wood was present were included, and the overall spatial patterns of source TEQ concentrations (see Section 8.3 for a discussion of source TEQ contributions and spatial patterns) were similarly unaffected by the exclusion of possible charred wood samples. Therefore, charred wood was determined not to be a significant confounding factor and potential charred wood samples were not excluded from the data evaluations.

After selecting a sampling location at a property, five subsample points were established and marked on the ground using pin flags. The default design included the four corners and center of a 10–by-10-foot square. Most residential yards accommodated this design; however, modifications were made by field personnel using their best judgment (discussed in Section 4.2).

Detailed methods for soil sample collection are provided in the SQAP (E & E 2008c). In summary, at each sampling location, groundcover was removed and then soil was collected from a depth interval of 0 to 3 inches beginning at the surface soil or humus horizon. Each sample consisted of a composite of five subsamples. Un-sieved soil samples from each subsample location were homogenized and then spooned into sample jars provided by the analytical laboratories. Soil characteristics, location sketch, and other pertinent descriptive sample information was recorded on field sample data sheets. Sampled holes were backfilled and groundcover was replaced once samples were collected. A clean, dedicated stainless steel sampling bowl and spoon were used at each sample location.

4.2 Deviations from SQAP

The following deviations from the SQAP are noted:

- The 10-foot-square subsample configuration was modified at 29 of the 85 sample locations, as summarized in Table 4-3. Modifications were made to avoid the presence of charred wood, to fit within a limited sample area, or to gain better access in densely forested areas. If charred wood was found in a subsample, the subsample location was moved several feet to find an area with no charred wood. In areas with limited sample area or along a bluff, the subsamples were occasionally collected along a straight line with 10-foot spacing. In some densely forested areas, the square was expanded to 20-foot spacing.

- The SQAP included use of a clean piece of aluminum foil placed at the bottom of each subsample hole. The purpose of the foil was to catch scrapings from the sidewall that fell off the sampling spoon. This procedure was eliminated from the sampling protocol because during preliminary test sampling, organic debris from above and loose material from the sidewall fell into the hole and onto the foil. This material was not uniformly representative of material scraped from the sidewall and was not appropriate for sample collection.
- The SQAP specified two project sample containers, including one 4-ounce jar for TOC analysis and one 8-ounce jar for dioxin/furan analyses. A split sample collected by a Rayonier representative required filling an additional 8-ounce jar, which was not discussed in the SQAP. As the analytical laboratory instructed, the two 8-ounce jars were each filled with approximately 6 ounces of soil. Approximately 16 ounces of soil were needed to fill the three sample containers, so a 4-ounce jar was used to collect soil at each subsample location instead of the measuring cup specified in the SQAP.
- No foil was used to cover the bowls, as described in the SQAP. It did not rain during sample collection and the bowls were constantly being filled or mixed prior to filling the sample containers, eliminating the need for the foil.
- A second field mobilization was scheduled in November to obtain an additional seven samples. During this second mobilization, cultural and historic resources monitoring was conducted by either LEKT or City of Port Angeles archaeologists.
- Of the 14 forest-type samples, five samples (E206SS, E402SS, E403SS, E498SS, and W299SS) were collected to satisfy grid cell location criteria but because they were obtained from forested areas, were re-classified after the field sampling event as forest-type samples.
- Due to limited access and/or suitability of properties in the eastern sampling zones, some grid cells were sampled more than once to maintain spatial coverage and sample counts within each zone. An attempt was made to collect samples as close as possible to the corresponding grid cell when that grid cell did not have accessible or acceptable properties.
- One sample from Zone W2 (W209SS) was collected south of the actual zoned area due to a lack of other suitable properties in grid cell W2-9 and the desire to maintain gridded coverage west of the former mill.
- One sample from Zone E1 (E199SS) was collected west of the actual zoned area to increase coverage in the vicinity of the former mill.
- One sample from Zone E3 (E302SS) was collected south of the actual zoned area to increase coverage of the eastern soil dioxins/furans study area resulting from a lack of properties meeting sample location criteria.
- One sample from Zone E4 (E402SS) was collected south of the actual zoned area to increase coverage of the eastern soil dioxins/furans study area.
- One sample in upslope transect T1 (T104SS) was collected north of the transect area boundary due to limited property access within the T1 upslope transect area. One sample

in transect T3 (T303SS) was collected slightly outside, to the west, of the transect boundary due to limited property access within the transect area.

4.3 Cultural and Historical Resources Monitoring

The cultural and historical resources monitoring protocols implemented for the project were consistent with the Lower Elwha Klallam Tribe Monitoring and Discovery Plan. Cultural resources monitoring procedures were approved during meetings between E & E archaeologist Sandra Pentney, LEKT archaeologist Bill White, and City of Port Angeles archaeologist Derek Beery on May 1, 2008, and are provided in the SQAP (E & E 2008c). A complete summary of the cultural resources monitoring activities is provided in Appendix A.

In preparation for this project, a cultural resources records search was conducted at Washington state’s Department of Archaeology and Historic Preservation (DAHP) to identify previously recorded resources in the area. The data recovered during this search were used to plan the sampling procedures to avoid known cultural resources. The soil sampling plan was biased toward choosing locations that were the least disturbed, increasing the likelihood that cultural resources could be encountered.

The intent of the cultural resources monitoring was to have a qualified archaeologist present during the collection of soil samples to protect cultural resources from disturbance. During the field sampling, each sample site was visually inspected by the archaeologist to ensure there were no surface signs of cultural resources. If there were no signs, then the archaeologist dug, or monitored the digging of, five subsample location holes in a confined area. The holes were oriented as described in Section 4.2. The soil removed from the holes was examined prior to side-wall sample collection to ensure that cultural resources were not present. In addition, the subsample collection and homogenization activities were monitored by the onsite archaeologist to ensure that artifacts were not inadvertently collected with the spoon. Photographs and field recording forms were used to document conditions at each sample location.

When a cultural resource was discovered, DAHP isolate and/or site recordation forms were completed, the find was photographed, and the artifacts were reburied on site. These forms were submitted to the DAHP for their archives, and copies of the forms were also provided to the landowners.

Cultural resources were identified at four sample locations, resulting in relocation of subsamples to alternate locations on the same property. All of the resources discovered during the project represent the historic era of Port Angeles and include fragments of historic stoneware and ceramics, a piece of terra cotta tile, a piece of red brick, and an overgrown, historic road with an abandoned 1940s- to 1950s-model Chrysler Corporation automobile.

While four sample locations yielded historic artifacts, these resources may not yield information pertinent to interpreting the past of the Port Angeles area. Maker’s marks or patterns on brick and household items are usually used to identify the approximate age of an artifact or relative date of the site. There were no maker’s marks or distinguishing patterns available on any of the construction or houseware artifacts that were recorded.

The historic road does not show up on historic maps available at the Port Angeles Library or on historic maps found online. A 1955 road map of the sample area, shown in Appendix A, does not show a road that corresponds with the location of the road in question. There is no way to establish when the car was abandoned at its current location.

While the cultural resources monitoring did result in the recordation of four cultural finds, the finds offered little information on the history of the area. These resources are not likely to be considered findings of significance.

4.4 Sample Collection Summary

A total of 85 samples were collected from seven gridded zones and three upslope transects. Four sample types were collected, including 60 grid-type samples, 14 forest-type samples, two roadside-type samples, and nine upslope transect-type samples. The distribution of these samples is provided in Table 4-1 and a more detailed summary is provided in Table 4-4, listing distance and direction of sample locations from the former Rayonier Mill HFB.

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5.0 Sample Analysis and Data Validation

5.1 Laboratory Analysis Results

All soil samples were analyzed for dioxin/furan congeners, dioxin/furan homolog groups, and TOC. Dioxin/furan analyses included quantification for the 10 homolog groups and 17 congeners with chlorine substitution in the 2, 3, 7, and 8 positions using EPA Method 1613B. Axys Analytical Services Ltd. (Axys) of Sidney, British Columbia, provided the final results of dioxin/furan analyses on January 2, 2009.

TOC was measured in all off-property soils sampled in this study to allow for evaluation of the relationship between dioxin/furan concentrations and soil TOC. Analytical Resources Inc. (ARI) of Tukwila, Washington, provided the final analytical results for TOC analyses on December 12, 2008.

The full analytical data reports are provided on disc as part of Appendix B to this report.

5.2 Data Validation

All analytical data for investigative and field replicate samples and laboratory quality control data were submitted to EcoChem Inc. of Seattle, Washington, for full data validation. Data were validated following the guidelines outlined by EPA's Analytical Operations/Data Quality Center, *National Functional Guidelines for Chlorinated Dioxin/Furan Data Review* (2005), *National Functional Guidelines for Superfund Organic Methods Data Review* (2007b), and *EPA Region 10 SOP for the Validation of Polychlorinated Dibenzodioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data* (1996).

EcoChem assigned data qualifiers to assist in proper data interpretation. A summary of the data validation results follows:

- Holding Times and Sample Receipt – No issues.
- Laboratory Blanks – No data were qualified based on method blank contamination.[7]
- Labeled Compounds – No qualifiers were assigned based on laboratory quality control sample results.
- Field Replicates – The absolute difference values between investigative and field replicate sample results were within control limits.
- Compound Identification – Several dioxin/furan analyte results were qualified by the laboratory as "estimated maximum possible concentration (EMPC)." This means that the result did not meet analyte identification criteria, which is often attributable to

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[7] "B" flags noting the presence of laboratory blank contamination assigned by the analytical laboratory were inadvertently left in the final data tables (Table 2-1) published with the *Data Summary Technical Memorandum* (E & E 2009). These data qualifiers were removed by the data validation subcontractor because identifiable concentrations were sufficiently greater than blank contaminant concentrations, meeting all quality assurance/quality control criteria.

interference from another compound. The EMPC-qualified results were assigned a "U" qualifier, denoting that the analyte could not be identified, i.e., was not detected.

In addition, all results for 2,3,7,8-TCDF were confirmed via a second analysis as required by the analytical method. The results from the initial analysis were qualified as "DNR" to note that they should not be reported. Results from the second, confirmatory analyses are included as usable data.

- Calculation Verification – No calculation errors were found. TEQs were calculated using TEFs provided by Ecology (2007; Van den Berg et al. 2006). TEQs were calculated by the laboratory two ways: (1) assuming "U" (nondetect) congeners were equal to a concentration of one-half of the sample-specific estimated detection limit (EDL), and (2) assuming nondetect congener concentrations were equal to a value of zero. These calculations are presented in the laboratory and data validator results spreadsheets.

EcoChem determined that all data are acceptable for use as qualified. Table 5-1 presents validated investigative sample results for dioxin/furan and TOC analyses. The type of sample (grid, forest, roadside, upslope transect) and distance and direction of the sample location relative to the former Rayonier Mill HFB also are listed in this table.

Table 5-1 does not include laboratory and field-collected quality control sample results or results of initial analyses for 2,3,7,8-TCDF. Field replicate samples with identification numbers ending with the letters "RP" and both initial and confirmatory 2,3,7,8-TCDF analyses are listed in the data tables from the lab and data validation contractor, provided in Appendix B.

Some TEQ concentration calculations from the laboratory do not assume that EMPC-qualified results are nondetect results. When sample results included EMPC-qualified values, the TEQ concentrations from the laboratory were recalculated by E & E based on the assumption that EMPC-qualified results were nondetect results, and that the EMPC-qualified value was a sample-specific detection limit (SDL). Consistent with calculations for other nondetect results with EDLs, EMPC-qualified results were included at one-half the EMPC value for TEQ calculations for final data evaluations. The consequence of this revision is that the TEQ results for some samples (see Table 6-3) are slightly different than the calculated TEQ results provided in the laboratory and data validation contractor data tables.

When the laboratory qualified a congener as nondetect, the laboratory used the sample-specific EDL in TEQ calculations. Use of the EDL for nondetect results was not modified by E & E when creating the final working database. Because the working database E & E used for data evaluation relies on the EDL and in some cases the SDL for EMPC-qualified values, the term "detection limit," or DL, will be used to collectively refer to the EDLs and SDLs used in the working database.

The final data validation report provided by EcoChem and the electronic database are provided on disc as part of Appendix B to this report. Validated data also are available on Ecology's Environmental Information Management (EIM) system.

6.0 Data Summary

Several different metrics, or standards of measurement, can be used to characterize dioxin/furan measurements. One metric, calculated TEQ concentrations and the contributions of various congeners to TEQs, is used here to illustrate some characteristics of the dataset. Statistical, spatial, and chemical patterns are summarized, based on sample total TEQ results. More detailed interpretation of the results is provided in Sections 7 and 8, including unmixing evaluations that partition total TEQ results into contributions from different sources.

6.1 Summary Statistics

Summary statistics for TEQ results are presented in Table 6-1. This table includes the minimum and maximum detected TEQ concentrations, location of the maximum detected TEQ concentration, mean TEQ concentrations, and number of samples exceeding the MTCA soil cleanup value of 11.1 ng TEQ/kg. The statistics are provided for the entire soil dioxins/furans study area as well as for individual sampling zones, roadside areas, upslope transect areas, and forested areas. For calculation of the TEQs, nondetect congeners were assumed to equal a value of one-half the detection limit. Nondetect results were infrequent in the dataset, and detection limits achieved were low. As a result, the calculated TEQs were relatively unaffected by how nondetect results were handled, as shown in Table 6-1 by the comparison of study-wide results using zero versus one-half the detection limit as substituted values.

Table 6-1 shows that 47% (40 of 85 samples) of the TEQ results exceed the default unrestricted land use MTCA cleanup value of 11.1 ng/kg. Mean TEQ concentrations calculated for each of the urbanized western zones (W1, W2, W3) ranged from 12.7 to 18.7 ng/kg, while mean TEQ concentrations calculated for each of the less developed eastern zones (E1, E2, E3, E4) ranged from 8.03 to 12.4 ng/kg, as shown in Table 6-1.

Table 6-1 shows that the mean TEQ concentration in the forested areas within the eastern zones (15.8 ng/kg) was greater than the mean for all eastern zone grid-type samples (11.2 ng/kg). The mean concentration for forest-type samples is similar to the mean for the urbanized western zones (16.0 ng/kg). The lowest TEQ concentrations were observed in the upslope transect areas, with a mean of 2.14 ng/kg.

A histogram showing the number of samples with TEQ concentrations falling into various TEQ concentration ranges is presented in Figure 6-1. TEQ concentrations presented in this figure are based on the assumption that nondetect congeners are equal to a value of one-half the detection limit.

6.2 Manipulation of Data

The validated laboratory analytical results provide bulk congener and homolog concentrations. Normalized values, showing the relative (fractional) contribution of each analyte to total concentrations, eliminate the effects of magnitude and show patterns more directly. Table 6-2 provides normalized congener and homolog results for all samples, in which each congener bulk concentration has been compared with the total of all congeners; homologs have been compared similarly.

Dioxin/furan bulk congener concentrations for each sample also were multiplied by the appropriate TEF, shown in Table 6-3. The sum of these weighted values is the TEQ concentration. TEQs are presented in three ways in Table 6-3: (1) nondetect congeners equal to the DL, (2) nondetect congeners equal to zero, and (3) nondetect congeners equal to one-half of the DL. Due to the low frequency of nondetect congeners across the entire dataset, the various TEQ calculation methods yield similar results. TEQ concentrations (assuming nondetect concentrations are equal to one-half of the DL) are depicted for the entire soil dioxins/furans study area in Figures 6-2 through 6-5.

The TEF-scaled concentrations presented in Table 6-3 were normalized by total TEQ concentrations (where nondetect congeners are equal to one-half the DL); the results are shown in Table 6-4. These fractional contributions of each congener to the total sample TEQ concentration are used to illustrate TEQ chemical patterns across samples, eliminating the effects of variations in TEQ magnitudes.

TOC was measured for each collected soil sample. While TOC has often been cited as one determining factor for soil dioxin concentrations, studies in the literature of the relationship between TOC and dioxin/furan TEQ have shown mixed results. The results for TOC (Table 5-1, TOC as percent) and TEQ (Table 6-3, TEQ as ng/kg using ND = 0.5 * DL) for all 85 samples in this study are graphically related in a scatter plot shown in Figure 6-6(a). The type of sample (grid, forest, roadside, upslope transect) is distinguished by color, according to the key shown in Figure 6-6.

Figure 6-6(a) readily demonstrates that there is no substantial relationship between TOC and TEQ for the samples in this study taken as a whole. A few apparent outlier values are noted, but the majority of samples, with TOC values between about 2% and 8%, are well distributed across TEQ values up to about 30 ppt.

A number of factors other than TOC are also likely to control dioxin concentrations in surface soils; thus, soil dioxins reflect a multi-factor and not a single-factor effect. When all the results from this study, over an area of more than 4 square miles, are combined in a single analysis of the TOC-TEQ relationship, these other factors are very likely to act as confounding variables. For example, wholly apart from TOC levels, the soil location with respect to dioxin sources is expected to play a significant role in measured dioxin levels. The well-known urban-to-rural gradient in soil dioxin concentrations should not be expected to be matched by a similar TOC gradient. Land cover and land use type affect dioxin concentrations, so at adjacent open and forested areas with similar TOC levels, dioxins levels may vary independently of TOC. Property-specific sources of dioxins (e.g., burn barrels, disposal of fireplace ash, chemical use) can contribute to local variations in soil dioxin levels, unrelated to TOC levels. Similarly, property-specific histories of soil-disturbing activities contribute to variations in residual soil dioxin concentrations and can mask any TOC-TEQ relationship that might exist.

The influences of these other factors potentially affecting soil dioxin concentrations can be partially controlled by evaluating selected subsets of the data. Accordingly, samples of a single type, within a smaller restricted portion of the total sampling area (where the distances and directions from dioxin sources are similar), were examined. For the first evaluation of a selected subset, forest-type samples were selected to minimize the influence of property-specific source contributions and soil disturbance histories; these latter two factors are much harder to control for residential (grid) sample types.

Of the 14 forest-type samples, 13 were collected from within a portion of the eastern sampling zones (see Figure 6-7). A TOC-TEQ scatter plot for just those 13 forest-type samples is shown in Figure 6-6(b). This restricted subset of samples shows a very strong positive relationship between TOC and TEQ values, nearly linear except for one apparent high-TEQ outlier. That one sample, E403, was collected from just north of the Rayonier Mt. Pleasant Street landfill and may be affected by additional local dioxin sources. The range of TOC values for the 13 forest-type samples is 1.11% to 9.44%; the range of TEQ values is 4.02 to 40.5 ng/kg at E403, with the next highest TEQ at 34.2 ng/kg. A regression analysis of log TEQ versus linear TOC values is highly significant ($p = 0.0002$, $R^2 = 72\%$). Linear and log-log regression produced similarly significant results, and omitting sample E403 produced even stronger results, with R^2 values up to 88% indicating a very strong TOC-TEQ relationship.

The results from grid-type samples in sampling zone E1 (Gale's Addition, residential land use) were also evaluated as a second restricted area, single-sample-type data subset. A TOC-TEQ scatter plot for just those 19 samples is shown in Figure 6-6(c). The range of TOC values for these E1 grid-type samples is 2.85% to 7.73%; the range of TEQ values is 2.54 to 26.6 ng/kg. As noted above, the influence of property-specific sources and histories is not controlled for these grid-type samples, and the scatter plot demonstrates greater variations in the TOC-TEQ relationships. Regression analyses of all 19 samples produced positive but non-significant ($p>0.05$) TOC-TEQ slopes. Removing just one sample (E196) with high TOC and very low TEQ values from the analysis resulted in statistically significant p values, but with more modest R^2 values (about 26% to 28%) than for the forest data subset described above.

The evaluation of TOC versus TEQ for forest-type samples shows that a strong positive TOC-TEQ relationship can be demonstrated when other factors influencing soil dioxin concentrations are largely controlled. The weaker but still positive relationship shown for the Zone E1 grid-type samples suggests a positive TOC-TEQ relationship even for residential locations within a small area, but with more variation, likely due to property-specific factors that are not being controlled. The lack of a TOC-TEQ relationship for all sample results combined supports the conclusion that TOC is only one among several factors controlling surface soil dioxin concentrations.

6.3 Spatial Distribution of TEQ Concentrations

In addition to TEQ concentrations for each sample (see Table 6-3), the direction (in degrees) and distance (in feet) relative to the former Rayonier Mill HFB were derived for each sampling location (see Table 5-1). Direction and distance information was used to depict the spatial distribution of TEQ concentrations within the soil dioxins/furans study area. Figure 6-7 relates the sample locations for the entire soil dioxins/furans study area to the location of the HFB stack, based on distance and direction. A 2006 wind rose for the ORCAA Ediz Hook station (as shown in Figure 3-2) is included as a reference for the designated wind sectors and subsequent data plots; for a discussion of wind rose data, see Section 3.1.

Figure 6-8 provides an initial scatter plot of all TEQ concentrations by distance (in feet) from the former Rayonier Mill HFB. The type of sample (grid, forest, roadside, upslope transect) is distinguished by color, according to the key shown in the figure. The occurrence of one high outlier grid-type sample TEQ result, at over 70 ng TEQ/kg, is notable in Figure 6-8. A number of forest-type samples at distances of about 2 to 3 miles (10,000 to 15,000 feet) have comparatively high TEQ concentrations; the most distant upslope samples, by contrast, have notably low TEQ results. The two roadside-type samples are at the low end of the TEQ ranges for samples at similar distances. The most conspicuous feature of Figure 6-8, however, is the broad scatter of grid-type sample TEQ concentrations, especially within about a mile and a half, indicating that total soil TEQ concentrations are affected by more than just distance from the stack. TEQ concentrations exceeding the MTCA Method B value of 11.1 ng TEQ/kg are widespread (40 of 85 sampling locations) across the study area, as shown on Figure 6-2. Spatial patterns for dioxins/furans are discussed further in Sections 8.2 and 8.3.4.

The wind sectors (e.g., east, east-southeast, southeast) shown in Figure 6-7 were used to subdivide the total set of samples based on direction relative to the former Rayonier Mill HFB. The relationship between TEQ concentration and distance plus direction from that stack is further illustrated by scatter plots for the samples segregated by wind sector, as shown in Figure 6-9. The number of sampling locations per wind sector is in many cases rather small, constraining any interpretations of TEQ trends with distance. Several of the segregated TEQ versus distance plots suggest trends for grid-type samples, for example, trends with increasing distance that show decreasing TEQs for east-southeast, southwest, and west-southwest directions and increasing TEQs for the west direction. Overall, however, the addition of direction to distance does not produce a markedly better interpretation of soil total TEQ results.

Total TEQ spatial patterns are addressed in more detail in Section 8.2. The spatial patterns of soil dioxins/furans are further evaluated in Section 8.3.4 based on the separation of total soil TEQ results into contributions from individual source profiles rather than total TEQ.

6.4 Chemical Patterns of TEQ Concentrations

Chemical patterns in soil samples are illustrated using the fractional contributions of each of the 17 2,3,7,8-substituted congeners to total TEQ concentrations (as listed in Table 6-4). Figure 6-10 depicts these patterns for all samples as a series of line plots. Samples are grouped by sample type (grid, forest, roadside, upslope transect) and by study design sampling zone for the numerous grid-type samples. The 17 2,3,7,8-substituted congeners are ordered along the X-axis with dioxin congeners on the left, furan congeners on the right, and within each group an increasing number of chlorines from left to right. Many of the samples have relatively similar profiles; a subset has notably higher contributions to TEQ from the first congener, 2,3,7,8-TCDD. Closer examination of these line plots reveals variations in the fractional contributions from individual congeners, even when overall patterns appear similar. Soil dioxin/furan concentrations typically reflect the cumulative impacts of multiple sources. The TEQ profile information shown in Figure 6-10 is used as input to multivariate statistical analyses (unmixing analyses) to evaluate dioxin/furan source profiles and source contributions to samples (see Section 8.3). The line plots in Figure 6-10 provide a visualization of the information used to perform these statistical data evaluations (see also Appendix C).

7.0 Data Evaluation: Overview

7.1 Introduction

Various graphical and statistical approaches were used to evaluate the magnitude and source of dioxins/furans in Port Angeles surface soils. This section provides a preview of the entire data evaluation approach, and a discussion of the metric used for the chemical pattern evaluation. The role of additional datasets and information from other published studies in interpreting the data evaluation results is also defined. The overview provided here can serve as a point of reference for the detailed evaluation discussions in Section 8.

7.2 Overview

The evaluations of the Port Angeles soil sample results use multiple approaches. Figures 7-1 and 7-2 are schematic representations of the data evaluation process, showing its overall structure and the relationships among parts.

The Conceptual Site Model (CSM; E & E 2008a) for dioxins/furans in Port Angeles soils recognizes that multiple sources for dioxins/furans exist in the community and that dioxin/furan concentrations at any location are very likely to reflect the combined effects from more than one source. A primary objective of this study is to evaluate sources contributing to measured soil dioxins/furans. Evaluating total (bulk) congener concentrations or total TEQ values for source identification is subject to strong limitations, due to the multiple source contributions to each sample. A one-to-one correspondence between a soil sample and a single dioxin source profile cannot be expected when the soil sample reflects inputs from multiple sources, each with a different profile. Similarly, a spatial gradient (i.e., a trend in concentrations related to distance and direction) in dioxin/furan concentrations over the soil dioxins/furans study area cannot be expected if multiple sources at different locations contribute, to varying degrees, to the total sample concentrations. For these reasons, it is important to discern the component parts of total dioxin/furan measurements when performing source evaluations.

A multivariate statistical approach—an “unmixing model”—is used in this study to provide a mathematical decomposition of the soils dataset into a group of source profiles and the contributions of each source to each sample. This process is referred to as a chemometric analysis. Figure 7-1 provides a schematic view of the unmixing model approach, which is discussed in Section 8.3 and in greater detail in Appendix C. The unmixing model approach for this study combines the statistical techniques of Principal Components Analysis (PCA) and Alternating Least Squares (ALS) analysis.

The evaluations of the Port Angeles soil dioxin/furan data proceed along four lines of evidence:

1. The magnitude of dioxins/furans, measured as TEQs (exposure/risk and cleanup levels are expressed in TEQ units),
2. The spatial pattern of dioxin/furan concentrations in soil
3. The chemical patterns of dioxin/furan congener concentrations in Port Angeles soil samples and comparison with other available source profiles and datasets, and

4. A mass balance comparing the required mass emissions of dioxins/furans derived from soil sampling results with estimated cumulative mass emissions from potential Port Angeles sources.

A fifth potential line of evidence, temporal patterns, is not relevant for the soils data in this study but has been used in other studies, for example, for age-dated sediment cores or for air pollution studies in which short-term temporal patterns of wind direction and pollutant levels are correlated.

Figure 7-2 provides an overview of the data evaluations for the multiple lines of evidence (shown in the far left column) used in this study, with cross-references to the report subsection in which each evaluation is described. The mathematical decomposition of bulk dioxin/furan measurements into the separate source-related increments for each sample allowed for more detailed evaluations using source-related (as opposed to total) measurements. As a result, the figure shows that a line of evidence initially evaluated based on total TEQs was evaluated further using source increments. Thus, Figure 7-2 shows, from left to right, that an initial evaluation of magnitude using total sample TEQs was followed by an evaluation of source-related magnitudes, using source increments determined from the unmixing model.

The final column in Figure 7-2 indicates that interpretation of the purely mathematical unmixing model results required evaluation of additional information on sample attributes and numerous source profiles, as discussed in Section 7.4, below.

7.3 Metrics

Soil dioxin/furan analyses provide concentration data for a set of homologs and the 17 2,3,7,8-substituted congeners. Chemometric analyses of these results can use various metrics as the starting point, including homologs, bulk congeners, and TEF-scaled congeners that are summed to calculate TEQ values. When the focus of the evaluation is on patterns, values are often normalized to eliminate differences due to varying magnitudes. The values for individual variables can also be scaled (Morrison and Murphy 2005, Murphy and Morrison 2007, Johnson et al. 2007). Examples of data evaluations using various metrics and approaches are provided in the references cited above and other peer-reviewed publications.

Dioxin/furan measurements typically have substantially different patterns when expressed as bulk congeners than when they are expressed as TEF-scaled congeners; examples of these substantial differences are illustrated for source profiles in Appendix D. Ideally the model developed in an unmixing analysis would reproduce both the bulk congener and TEF-scaled congener profiles accurately, with small residuals (differences between modeled and measured values) for all congeners and all samples. However, a set of relatively small differences in one profile comparison can result in much larger differences for the second profile, because the TEFs that translate from one profile to the other range over multiple orders of magnitude. It has proven difficult to achieve very high goodness-of-fit results for both bulk and TEF-scaled profiles simultaneously in a single unmixing analysis with a constrained number of sources (the parsimony principle for modeling).

One metric, TEQ, is most relevant for exposure/risk assessments and cleanup decisions. The individual 2,3,7,8-substituted congener concentrations are scaled by TEF values, to reflect their varying potency, and the scaled values are summed to reflect the overall toxicity of the dioxin/furan mixture. The set of TEF-scaled congener concentrations provides a profile of the relative contributions of individual congeners to overall toxicity. From the point of view of risk estimates and cleanup decisions, the bulk dioxin/furan levels in a sample are of little importance if, after TEF scaling, they contribute almost nothing to TEQ concentrations. Examination of the TEF-scaled results for the Port Angeles soils dataset shows that there are several congeners that have this characteristic (compare Table 5-1 and Table 6-3, especially for the higher-chlorinated congeners; also, compare the bulk congener and TEF-scaled profile plots in Appendix D).

The definition of "dioxin/furan source" may seem straightforward, and singular, but careful reflection shows this not to be the case. Metrics are intimately bound up with the definition. Consider a set of dioxin/furan emissions sources with different characteristics, and how they would rank in magnitude. A source with the highest "total dioxins/furans" (e.g., the sum of a complete homologs profile) but modest 2,3,7,8-congener emissions would rank at the top for homologs but lower for total (bulk) 2,3,7,8-congeners. Similarly, a source with high emissions of 2,3,7,8-congeners but mostly those with very low TEFs, producing only a modest TEQ value, would rank at the top for summed 2,3,7,8-congeners but lower for TEQs. In one sense—the measurement of all individual dioxin/furan congeners—there is one physical reality for source emissions. From the perspective of source identification/source ranking, however, there is a reality corresponding to each of the metrics that can be used. When it is not possible to achieve equivalent goodness-of-fit to sample profiles for both bulk congeners and TEF-scaled congeners, chemometric analyses require a choice of metric. For this study, unmixing analyses were based on TEF-scaled 2,3,7,8-congeners because exposure/risk assessments and cleanup decisions are based on TEQ values, and because this approach produces the best goodness-of-fit for sample TEQ profiles. The "dioxin/furan sources" of greatest interest to meet the objectives of this study are those that contribute to the TEQ profiles observed in collected soil samples.

This approach using normalized TEQ profiles has been used in other studies for dioxin/furan data evaluations (Lohmann and Jones 1998, Alcock et al. 2002, Hilscherova et al. 2003, and Demond et al. 2008).

A measure of the performance of analyses based on the TEF-scaled congeners metric is the interpretability and consistency of the chemometric results, as presented in Section 8. Additional evaluations using other metrics are not precluded, and in fact some exploratory analyses using other metrics were performed during data evaluations (Appendix C).

7.4 Additional Datasets for Interpretation

The unmixing model provides a mathematical decomposition of the soil dioxin/furan dataset for Port Angeles, but by itself does not interpret those results; it is purely a mathematical tool. A substantial effort was made to compile comparison datasets and additional information to support the interpretation of sources. Several hundred additional TEQ component profiles were gathered and used to support interpretation of the unmixing model results. Sources of the comparison profiles are provided in Section 8.3.1 (see also Appendix C). In particular, stack test data were collected for multiple HFBs where salt-laden wood was burned to better characterize that source profile.

The Port Angeles soil dioxin/furan results were compared with other soils datasets to determine the degree to which they were similar or dissimilar. These comparisons first focused on soil TEQ concentrations (magnitude), and subsequently on TEQ component profiles (pattern). The source profiles for TEQ composition identified by the unmixing model were compared with an extensive inventory of source profiles, including HFBs, to interpret the modeled profiles and determine whether sources existed within the soil dioxins/furans study area for which the model source profiles were representative.

8.0 Data Evaluations: Results

8.1 Magnitude

The concentrations for the 17 2,3,7,8-substituted dioxin/furan congeners were converted to total TEQ values using Ecology's recommended TEFs (Ecology 2007; Van den Berg et al. 2006). The total TEQ results for the 85 soil samples collected for this study ranged from 0.80 to 76.3 ng TEQ/kg (or ppt), dry weight (dw). Nondetect congener results were very infrequent and made little difference in the calculated TEQ results. For the data evaluations presented here, nondetect results were included in TEQ calculations at one-half the reported detection limit.

A summary of these TEQ results was presented in Section 6.1. This section provides a more detailed evaluation of TEQ magnitudes by sample type. The Port Angeles results are also compared with results from a number of other soil dioxin studies to place them in context and assess whether they are typical or atypical. All the evaluations in this section are based on total TEQ measurements. Based on unmixing analyses of chemical patterns (see Section 8.3), portions of the total sample TEQs associated with specific source patterns (i.e., a partitioning of total TEQ) were determined. Those source-related TEQ magnitudes are discussed in Section 8.3.3.

As noted in Section 6.1, almost half of the samples in this study exceed Ecology's Method B value of 11.1 ng TEQ/kg. Evaluations of total TEQs are most relevant for comparisons with this value. Evaluations of source-related TEQs (Section 8.3.3) are important for interpreting sources contributing to the total measured TEQs.

The Port Angeles study soil samples included a number of different types of sampling locations. The type of sampling location, and its associated location, land uses, land cover, and property history, are known to affect contaminant concentrations. It is therefore important to look at TEQ magnitudes (concentrations) separately for each sample type.

The sampling design included grid-type sampling over the soil dioxins/furans study area for all samples not otherwise targeted as forest, roadside, or upslope sample types. In a few cases grid-type samples were collected from locations with forest cover, consistent with the sampling design principles. Those few samples that were initially characterized as grid-type samples for the study design are included in these data evaluations as forest-type sampling locations. The nine upslope samples also include a few forested locations, with most upslope locations being open fields. Upslope samples are all retained as a single sample type reflecting this mix of locations because of the dominance of location (including elevation) and land use (non-urban) features for that data subset. Finally, the largest data subset of grid-type samples represents mostly residential yard locations, with a smaller fraction of open space locations (fields).

Box-and-Whisker Plots

Box-and-Whisker plots provide a way to visualize major features of the distribution of datasets. They can be used to quickly compare multiple related datasets.

The central box in a Box-and-Whisker plot encloses the middle 50% of the distribution (25th to 75th percentiles), with the median value (50th percentile) shown as a line inside the box. The mean value can be shown as a point value, not equal to the median value if the distribution is not symmetric.

The whiskers extending from the box are drawn to the smallest and largest values in the dataset that are within 1.5 interquartile ranges of the 25th and 75th percentile box endpoints. (The interquartile range is the difference between the 75th and 25th percentile values). Additional, more extreme values beyond the whiskers are plotted individually. When such point values are more than three interquartile ranges beyond the central box limits, they are marked with an additional "plus" symbol.

NOTE: Because of slightly different formulas used for calculating percentiles, different statistical software can produce slightly different (interpolated) percentile values. The Box-and-Whisker plots and 75th percentile values (Table 8-1) used in this report reflect values from Statgraphics Plus software.

The statistical distributions of total TEQ by sample type are summarized using box-and-whisker plots in Figure 8-1 [for a description of box-and-whisker plots, see the text box on this page]. The number of samples for each sample type, the range of total TEQ values, and the median and 75th percentile values for the data collected in Port Angeles is provided in Table 8-1. Similar summary information for other comparison datasets is also included in Table 8-1 and discussed below.

The lowest total TEQ results are for the upslope transect-type samples (n = 9; median = 1.82 ng TEQ/kg). Those samples were collected from sites with elevations of about 570 to 1,110 feet, well above all remaining sampling locations. While not totally undeveloped, the upslope sampling area represents the most rural, least urbanized portion of the soil dioxins/furans study area.[8]

Only two targeted roadside-type samples were collected, both adjacent to the most heavily traveled road in the region (Highway 101) and east of the most heavily developed areas of Port Angeles. The total TEQ values (4.04 and 6.50 ng TEQ/kg) are intermediate between the upslope and grid or forest locations. This data subset may underestimate the full range of typical roadside TEQs due to the small number of samples (n = 2). The main reason for targeting a few roadside-type samples was to develop a site-specific TEQ profile for that sample type. Vehicle emissions from fuel combustion are a known source of dioxins (see Appendix D) and contribute to general urban dioxin profiles. The two roadside-type samples in this study provide an initial characterization of roadside soil dioxin profiles. They did not define a unique profile in the unmixing analyses (Section 8.3), but appear to have been subsumed within the general urban profile.

The grid (n = 60, median = 11.87 ng TEQ/kg) and forest (n = 14, median = 10.61 ng TEQ/kg) sample types have similar median values, but the distribution of higher forest TEQs is shifted upward compared with grid-type samples. Comparisons between grid and forest sample types must consider the different spatial coverage for these two datasets. The grid-type samples include

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[8] Upslope sample T201SS was collected close to the Daishowa (Lawson) landfill. That sample had the highest TEQ at 5.54 ng TEQ/kg, more than twice the second highest upslope value. It is possible that the T201SS result was elevated by landfill operations, making it less representative of typical upslope values.

much of the most heavily developed urban core of Port Angeles as well as less developed areas to the east. With the exception of a single forest-type sample along upper Lauridsen Boulevard (W299), all of the forest-type samples were taken from the less developed eastern end of the soil dioxins/furans study area at generally greater distances from the former Rayonier Mill site. Based on the available wind rose data, the dominant downwind directions from the former Rayonier Mill are to the east/southeast (see Section 3.1), where almost all the forest-type samples were collected. Further detailed comparisons between similarly located grid- and forest-type samples can be made when spatial patterns in results are evaluated ("type within location" analyses, Section 8.3.4).

A gradient of decreasing TEQ concentrations is generally recognized from urban to rural to remote locations (Cleverly et al. 2003). The much lower TEQs for upslope locations in this study are consistent with that gradient. Forest soils are also known to show increased TEQ concentrations compared with nearby non-forested locations (Horstmann et al. 1997, Mclachlan and Horstmann 1998, Horstmann and McLachlan 1998, Wania and McLachlan 2001, Schmid et al. 2005, Schumacher et al. 2006). Considering the locations for forest-type samples in this study, outside the urban core, and the TEQ results for that sample type, an increased TEQ in forest soils appears to be confirmed. The locations where it was possible to include forest-type soil samples were very limited because of the extent of development over much of the soil dioxins/furans study area.

A relevant question about TEQ magnitudes is whether the results for this study reflect typical TEQ concentrations for a smaller urbanized area such as Port Angeles. A number of available datasets offer points of comparison. Figures 8-2 through 8-4 present comparative box-and-whisker summaries for selected datasets. The data sources and summary statistics for these studies are provided in Table 8-1. The TEF values used to calculate TEQ concentrations from bulk congener results have been modified several times in previous years. Given the various dates represented across comparison datasets, different sets of TEFs were used by the authors to calculate TEQs. The original bulk congener concentrations were used together with Ecology's current TEFs to recalculate all of the TEQ values discussed here, with the single exception of the Utah study, for which detailed bulk congener results were not available. In that case, the TEQs as reported by the authors are used. Cross-study comparisons are enhanced by putting the TEQ calculations on a consistent TEF basis. Even though these multiple studies are treated consistently for TEFs, there are other sources of variation that can affect cross-study comparisons; these are discussed further below.

One study is available that provides dioxin/furan sampling results for residential yards in Western Washington. As part of the site investigations of the Oeser Superfund site in Bellingham, Washington, background samples were collected from both residential yards and open areas (e.g., parks) within the City of Bellingham at some distance from a wood-treating facility (E & E 2002). Ten locations of each sample type were sampled. Additional residential properties located near the wood-treating facility were also sampled but those results are not evaluated here because of potential confounding by impacts from that facility.

The TEQ distributions for the Port Angeles grid-type samples and the Bellingham background samples are compared in Figure 8-2. The Bellingham lab analyses had substantially higher detection limits and a significant proportion of nondetect results. As a result, unlike results using the Port Angeles data, when evaluating the Bellingham data there is a sizable difference when TEQs are calculated assuming zero for nondetect results than when TEQs are calculated assuming one-half the detection limit for nondetect results. TEQ distributions for the Bellingham data are shown using both calculation approaches in Figure 8-2 and Table 8-1. Samples from open space locations have lower TEQ values than residential samples in Bellingham. The residential median value of 4.78 (ND = 0) to 7.32 (ND = ½ DL) ng TEQ/kg in Bellingham is lower than for the Port Angeles grid-type samples; in general, the Port Angeles distribution appears to be shifted higher compared with Bellingham's. Among the 10 residential sampling locations in Bellingham, one has a high outlier TEQ result (see Figure 8-2).

A number of additional datasets with dioxin/furan analyses for urban soils were located. They included the Washington state survey by Ecology (Rogowski et al. 1999); studies of the Denver metropolitan area (U.S. EPA Region 8 2001) and Davis County, Utah (University of Utah [undated]); a national survey of Australia (Muller et al. 2004); and a detailed study of Trondheim, Norway (Andersson and Ottesen 2007, Andersson 2009). Among the comparison studies, the Washington state survey had relatively elevated analytical detection limits and a high frequency of nondetect results. TEQ results calculated using one-half the detection limit for nondetect results are carried forward for the datasets from that study.

The Port Angeles grid-type sample results are compared with these five urban soil studies in Figure 8-3 and Table 8-1. Median TEQ values for the five comparison studies range from 0.90 to 4.18 ng TEQ/kg, versus 11.87 ng TEQ/kg for Port Angeles; 75th percentile values for the five studies are from 1.83 to 10.74 ng TEQ/kg, versus 17.45 ng TEQ/kg for Port Angeles. A small number of high outlier values occur in most of the comparison studies. The Bellingham background residential TEQ results are similar to these five urban comparison datasets, all shifted lower relative to Port Angeles grid-type samples.

A summary of residential soil sampling in two Michigan counties (Jackson and Calhoun), done for comparison with contaminated areas near Midland, Michigan, has also recently been published (Demond et al. 2008). Results for individual samples are not available. Samples were collected from 0 to 1 inch (n = 194) and 1 to 6 inches (n = 53). The median values for these two depth intervals were 2.9 and 6.8 ng TEQ/kg and the 75th percentile values were 5.7 and 8.7 ng TEQ/kg, respectively, as reported by the authors (using current TEF values). Those summary values are similar to the results from the urban comparison datasets evaluated here. Additional studies of urban soils in the United Kingdom (Creaser et al. 2007) and in Torino, Italy (Biasioli and Ajmone-Marsan 2007) have reported TEQs that are consistent with the results of the other cited studies for urban soils.

As seen in Figure 8-1, the Port Angeles forest sample types include some of the higher TEQ values, and the upslope transect-type samples have among the lowest values. The non-grid-type Port Angeles results (forest, roadside, and upslope sample types; see Figure 6-7) are compared with three other non-urban datasets in Figure 8-4 and Table 8-1. The Washington state survey (Rogowski et al. 1999) included sampling of forested and open locations, albeit not on the urban fringe. EPA has also recently completed soil sampling at rural locations that are part of the National Dioxin Air Monitoring Network (EPA 2007b). As with the urban comparison datasets, a small number of high outlier TEQ results occur among these non-urban datasets. The most rural part of the soil dioxins/furans study area, represented by the upslope transect sampling locations, is seen to have TEQ results similar to the Washington state open areas and the U.S. rural sampling locations. Measurable low TEQ concentrations are found even at rural and remote locations as a result of long-range transport of dioxins/furans. The Port Angeles forest sampling locations have TEQ results far higher than any of the three non-urban comparison datasets. A national survey of soils in Switzerland (Schmid et al. 2005) included 11 forest-type samples, which had a median value of 4.58 ng TEQ/kg and a range of 2.32 to 11.95 ng TEQ/kg. The Swiss results are also low compared with Port Angeles forest-type sample results.

Differences in the sampling and analysis protocols used for dioxin/furan studies can affect the resulting measurements. The multiple comparison datasets reviewed here differ in a number of characteristics, including, among others, the following: the sampled depth interval used to define surface soils; the use of grab versus composite sampling approaches, the details for composite sampling, and the spatial scale reflected in samples; the criteria for selecting sampling locations; the application of pre-analysis sieving and the particle sizes analyzed; the number of samples collected (representativeness of underlying distributions); the population, traffic density, land use, and similar characteristics of sampled areas; and the laboratory analytical detection limits achieved. Despite the variability in protocols across studies, it is notable that the TEQ distributions from multiple studies show a marked degree of similarity (see Figures 8-2 through 8-4 and Table 8-1). The TEQ distributions for Port Angeles grid- and forest-type samples appear to be shifted upwards when compared with the cumulative information from multiple comparison studies. A more definitive study of typical urban dioxin/furan TEQs in surface soils, absent notable impacts from point sources, is not available, particularly for Western Washington urbanized areas and for residential properties.[9]

Many studies of dioxins/furans in soil have produced datasets that are “right-skewed” (i.e., the mean is located to the right of the median concentration), with a few high outlier values. The Port Angeles results show one high outlier TEQ result of 76.3 ng TEQ/kg at W209 (a grid-type sample); the second highest result is 40.5 ng TEQ/kg at E403 (a forest-type sample). Most of the comparison datasets similarly have one or a few high outlier values. Where sufficient information on a property history and the activities of current and past occupants can be compiled, it is sometimes possible to identify the source(s) causing the high outlier result. Franzblau et al. (2009), for example, identify credible explanations for high outlier results at two properties in Michigan based on case study investigations. Some property-specific information was collected as access agreements for the Port Angeles study were being completed, but detailed investigations of those sampling locations with the highest TEQ results have not been undertaken.

TEQ magnitude summary. The approach and conclusions for the evaluation of the total TEQ results for Port Angeles soil samples are summarized as follows:

- Total TEQ results were variable, ranging from 0.80 to 76.3 ng TEQ/kg.
- A small number of high outlier TEQ concentrations occurred, consistent with observations in other soil dioxin studies.

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[9] Ecology is in the process of planning additional statewide studies of soil dioxins in both rural and urban areas, to be completed in 2011.

- TEQ concentrations in the most rural portion of the soil dioxins/furans study area—the upslope transects—were far lower than in the developed urban areas of Port Angeles.
- Almost half (40 of 85) of the samples had TEQ values exceeding Ecology's Method B value of 11.1 ng TEQ/kg, including 33 of 60 grid-type samples.
- TEQ comparisons across sample types are affected by differences in the sampled areas for each type. Upslope transect and roadside-type samples in this study had lower median TEQ concentrations than grid and forest sample types.
- Although median TEQs were similar for grid- and forest-type sample subgroups, forest-type samples included a number of the higher TEQ results. Elevated TEQs in forest soils (a consequence of land cover) are consistent with the site conceptual model, especially given the locations of most forest-type samples well outside the Port Angeles urban core.
- Compared with available soil dioxin results from other locations, which are reasonably consistent with one another, soil dioxin TEQs in Port Angeles appear to be shifted higher. This suggests that one or more local sources may have contributed to moderately elevated soil TEQs.
- TEQs for the upslope transect-type samples, well outside the developed Port Angeles area, are similar to Washington statewide and U.S. rural sampling results.

8.2 Spatial Pattern

An isolated source or a dominant source for dioxins/furans may produce a spatial pattern in nearby soils showing a clear relationship to that source. For an air emissions source, that pattern is typically decreasing concentrations with distance and a positive correlation with wind rose frequencies. Two types of confounding factors, however, often obscure spatial patterns in soil dioxins, especially in developed urban areas. First, dioxin sources rarely exist in isolation or at a magnitude that is truly dominant; soil dioxins almost always reflect the cumulative impacts of many sources. Numerous small point sources (e.g., boilers or other combustion sources) often exist over an extended area, and area sources (e.g., vehicle emissions) also contribute to area-wide dioxin impacts. Much of the total airborne dioxin loading is also not deposited locally (Lohman and Seigneur 2001). The second type of confounding occurs because property-specific factors, often occurring on a spatially random basis, can affect measured dioxin concentrations. Property-specific factors include a variety of soil-disturbing activities (e.g., tilling, soil removal or soil importation) that remove or dilute dioxins in surface soils, as well as activities (e.g., application of dioxin-containing chemical products, use of outdoor burn barrels, or ash disposal) that can significantly increase local dioxin levels. Differences in types of land cover also affect the degree of deposition of airborne dioxins.

An overall spatial gradient in soil dioxin concentrations (as total homologs, total congeners, or total TEQ) from urban to rural to remote areas has been well established in the literature, reflecting the greater number, magnitude, and density of urban sources for dioxins. Studies of substantial dioxin emission sources, however, have typically observed spatial patterns in soil dioxins (total TEQs) related to those sources only over relatively small areas and distances, if in fact any such patterns were detected at all. Tall stack heights leading to greater dispersion of dioxin emissions, as well as the confounding factors noted above, are likely contributors to this general finding.

The spatial distribution of soil total TEQ results in this study was briefly described in Section 6.3 and graphically summarized in Figures 6-7, 6-8, and 6-9. This section further discusses and summarizes spatial patterns based on total TEQ measurements. Dioxins measured as total TEQs, however, are particularly prone to confounding when used as a measure of source-specific impacts, since by assumption almost every measured soil dioxin value in urban areas is a composite of impacts from multiple sources, including diffuse regional sources. Unmixing analyses (see Section 8.3 below) model total TEQs as the combined contributions from specific sources or source profiles. The evaluation of those source-related “TEQ increments” provides a more refined tool for looking at spatial patterns and source identification. Those more detailed spatial pattern evaluations are presented in Section 8.3.4, after the unmixing analysis results are described. Previous studies appear to have focused on total TEQs and not “TEQ increments” when evaluating spatial patterns.

As noted in Section 6.3, distance versus TEQ and distance/direction versus TEQ scatter plots do not reveal much spatial structure in soil total TEQ concentrations (see Figures 6-8 and 6-9). A few of the distance/direction versus TEQ plots, which individually include small sample counts, suggest either increasing or decreasing trends with distance from the Rayonier HFB. A brief examination of distance/direction versus specific bulk congener plots (see Appendix C) similarly suggests various trends with distance. The evaluation of dioxin/furan data and source-sample relationships, however, is fundamentally a multivariate problem, so multivariate techniques (e.g., unmixing analyses as presented in Section 8.3 below) are more appropriate than single congener evaluations in determining patterns.

The distance versus TEQ scatter plot (Figure 6-8) shows the most distant upslope transect-type samples to have much lower total TEQ concentrations than almost any of the samples in urbanized areas of greater Port Angeles. This is consistent with the typical urban-to-rural gradients for soil dioxins. The broad scatter of total TEQs for grid-type samples in this scatter plot was already noted in Section 6.3. A distance versus TEQ scatter plot collapses a two-dimensional spatial analysis to one dimension, and “stacks” results for locations in different directions (with different wind frequencies) but at similar distances from the reference point— in this case, the Rayonier HFB stack.

Figure 8-5 is a two-dimensional dot map of TEQ values for all samples (n = 85). The different sample types are coded using different symbol shapes. Total TEQ values are shown in Figure 8-5 using color-intensity scaling with four levels, the highest being values greater than 11 ng TEQ/kg. Compared to similar dot maps in Section 6, Figure 8-5 uses a more detailed lower range of TEQ concentration intervals useful for comparison with later TEQ increment dot maps (see Figures 8-18 through 8-21).

A total of 40 out of 85 sampled locations have total TEQ concentrations exceeding the MTCA Method B value of 11.1 ng TEQ/kg (see Table 6-1 and Figure 8-5), of which 33 occur at grid-type locations (n = 60). While the overall appearance of the dot map is that values exceeding 11.1 ng TEQ/kg are widespread, close inspection indicates several features of interest. Three clusters of contiguous grid sampling locations exceeding 11.1 ng TEQ/kg can be identified: (1)

10 locations to the southeast of the Rayonier HFB, in the relatively densely developed residential area of Gale's Addition; (2) 11 locations to the southwest of the Rayonier HFB, near the Port Angeles central urban core; and (3) 8 locations farthest to the west and southwest of the soil dioxins/furans study area, in residential developments that are for the most part dense. (Note: the second and third clusters could also be considered a single cluster.) The remaining four grid locations exceeding the MTCA Method B value are two east of Gale's Addition (one near the extreme eastern end of the soil dioxins/furans study area) and two farther south of the Rayonier HFB. Areas east of Gale's Addition where land use transitions from denser residential areas to more rural areas are seen to have relatively few grid sample exceedances of the MTCA Method B value of 11.1 ng TEQ/kg; this is discussed in more detail in Section 8.3.4. In the more developed urban portion of the study area (western sampling zones), exceedances of the MTCA Method B value are widespread (21 of 32 grid-type sampling locations; see Figure 8-5).

In addition to the 33 grid samples above 11.1 ng TEQ/kg, 6 of the 13 forest-type samples in the east zones and the single forest-type sample in the west zones exceed that value.

A small number of high outlier total TEQ results for grid samples is also notable. Location W209, at 76.3 ng TEQ/kg, is a high outlier for the entire study. Location E499 with 19.9 ng TEQ/kg, at the eastern limit of the soil dioxins/furans study area, is a local high outlier compared with other nearby grid-type samples. Finally, in smaller local areas, closely spaced sampling locations have diverse total TEQ results, illustrating that relatively high local variability in soil dioxin concentrations can occur.

The two-dimensional dot map and the distance versus TEQ scatter plots referenced in Section 6 are consistent with overall spatial patterns for total TEQ concentrations in soils. Apart from the urban-to-rural gradients demonstrated clearly by the upslope transect results and also supported by the results from the easternmost grid-type sampling locations (see Section 8.3.4 below), total TEQs do not exhibit simple gradients or spatial trends and do not show clear patterns related to identified potential sources (compare with Figure 2-1).

As mentioned above, the unmixing model estimates the contribution of separately identified sources to each sample TEQ, and further evaluation of spatial patterns for source-related TEQ increments, rather than total TEQs, is discussed in Section 8.3.4.

Total TEQ spatial pattern summary. The approach and conclusions for the evaluation of spatial patterns of soil dioxins based on total TEQ concentrations are summarized as follows:

- Distance and distance/direction versus TEQ scatter plots (one-dimensional) and a dot map (two-dimensional) were used to evaluate spatial patterns for total TEQ results.
- The expected difference in total TEQ concentrations between urban and rural areas was confirmed, with markedly lower values for the upslope transect locations compared with urbanized areas of Port Angeles, and generally lower values in the less-developed easternmost sampling areas.
- Apart from the urban-to-rural gradient, no simple gradients or trends were evident for total TEQs within the urban portion of the study area, even if the evaluation was limited

to only grid-type samples (n=60) to reduce potential confounding from multiple sample types.

- Instances of high local variability in total TEQs for closely spaced sampling locations occurred, consistent with the conceptual model of comparatively high variability in developed areas where soil-disturbing activities and property-specific dioxin sources are likely.
- A few high-outlier total TEQ results appear anomalous compared with other nearby sampling locations.
- Grid-type sampling locations that exceed the MTCA Method B value of 11.1 ng TEQ/kg are widespread in developed areas of Port Angeles.
- The absence of clear spatial patterns in total TEQs that can be related to any single dioxin emissions source is influenced by the contributions from multiple dioxin sources across Port Angeles, as well as by varying individual property histories (soil-disturbing activities that dilute or reduce accumulated soil dioxin levels, and property-specific dioxin sources).

8.3 Chemical Pattern

The assumption underlying analysis of chemical patterns is that every sample potentially reflects the combined effects from multiple sources of dioxins/furans; many sources for dioxins/furans in the environment have been identified. Multivariate statistical techniques were used to deduce the mixture of source contributions to the measured dioxins/furans in Port Angeles soils. This statistical partitioning of measured total TEQs in soil samples is referred to here as an unmixing model.

Mathematical techniques to accomplish unmixing of composite datasets are not new, but they are finding increasing application in environmental studies, especially over the past 10 years or so (Morrison and Murphy 2005, Murphy and Morrison 2007, Johnson et al. 2007). There are several mathematically distinct methods for conducting unmixing analyses. These various approaches are reported to produce similar results when applied to the same dataset, so the choice of methodology is not critical. Unmixing models can be applied to several different metrics, all developed from the same set of reported measurements. In this study, a combination of principal components analysis (PCA) and alternating least squares (ALS) is the primary approach for an unmixing analysis; some additional methods, such as hierarchical cluster analysis (HCA), are also used (see Appendix C).

Normalized TEQ values for the 17 2,3,7,8-substituted congeners, also referred to as TEQ component profiles, are the primary metric used in this study, although exploratory evaluations using other metrics were also performed. The sample analyses for this study achieved low detection limits. As a result, there are very few nondetect results for individual congeners, and the evaluations of TEQ profiles are not confounded by nondetect results.

Details of the chemometric analyses for unmixing and source identification are provided in Appendix C. The chemometric analyses are summarized here, focusing on the primary methods used (Section 8.3.1) and the main results (Section 8.3.2). Analyses of chemical patterns consist of two equally important parts:

- Decomposition of the Port Angeles soils dataset into its components (i.e., unmixing), and
- Interpretation of the sources mathematically identified by the unmixing analysis.

As noted previously, interpretation of modeling results involves additional datasets beyond the soil samples collected for this study. Additional data used in interpreting the unmixing model results included additional soil dioxin studies (primarily urban soils, but also forest and rural soils) and profiles of known and characterized dioxin sources (mostly air emission sources, especially HFBs burning salt-laden wood, but also chemicals whose direct application could introduce dioxins/furans into soils).

The main products of the unmixing analyses, which provide a framework for detailed discussions include the following:

- A determination of the number of sources required to account for most of the variance in the dataset;
- A chemical profile (for this study, a TEQ component profile) describing each of the identified sources;
- The fractional contribution of each of the identified source profiles to each sample;
- A characterization of the model's goodness-of-fit through residuals measurements for each sample; and
- Comparisons of the study samples and the individual source profiles with other available profiles, to support source identification.

The unmixing model approach is a type of receptor modeling. It does not require knowledge of potential source patterns in advance, but determines candidate source patterns using only the soil sampling results. Once those source patterns are defined, attempts are made to interpret them and identify likely sources for the area being studied. A type of "forward" analysis (termed target testing), starting with candidate source profiles, was also performed as an additional evaluation, but is not described further in this section (see Appendix C for details).

For the mathematical calculations in an unmixing analysis, the sample data are treated purely as numbers stripped of all other attributes. No information on sample spatial locations, land use, land cover, property history, proximity to roads or other features, or similar characteristics of the samples influences the mathematical solution to the unmixing problem. The unmixing results, however, can be reviewed with respect to all of these attributes of samples to support interpretation of the results and determine whether the source identifications are meaningful for the soil dioxins/furans study area. Consistency of the unmixing decomposition of sample measurements with known characteristics of the samples and the soil dioxins/furans study area is one important measure of the validity of data interpretations.

The results of the unmixing model, with a decomposition of each sample into contributions from separate sources, are used for more detailed evaluations of dioxin/furan magnitudes (see Section

8.3.3), spatial patterns (see Section 8.3.4), and a dioxin/furan mass balance (see Section 8.4). The analyses of chemical patterns therefore have a central role in the overall evaluations of the Port Angeles soils data.

8.3.1 Methods

This section provides a basic description of the methods used for the unmixing analyses, the expanded datasets compiled to support interpretations of the unmixing model results, and sources of uncertainty in unmixing analyses.

Unmixing analyses. TEQ component profiles for each sample were developed from the analytical results for bulk congener concentrations. Using Ecology's current TEF values (see the MTCA Cleanup Regulation, WAC 173-340-900, Table 708-1; TEFs adopted from Van den Berg et al. 2006), the total TEQ for each sample was calculated and the contribution from each congener was then normalized by dividing by the total TEQ. After normalization, the sum of the contributions from the 17 2,3,7,8-substituted congeners was 1 for each sample. The primary unmixing analyses were based on this set of TEQ component profiles (Table 6-4 and Figure 6-10), which focus on the patterns (i.e., composition) rather than the TEQ magnitudes of samples.

With 17 2,3,7,8-substituted congeners defining the chemical patterns in the sample profiles, each sample can be visualized or mapped as a point in a 17-dimensional space. Samples with similar TEQ profiles would be located near one another in that 17-dimensional space. A principal components analysis (PCA) attempts to reduce the number of dimensions required to map the data, while accounting for almost all of the variability in the dataset. PCA factors, each representing some combination of the congener variables, are determined, with each added factor accounting for successively less of the overall variance. A decision on how many factors to retain in the model of the data is made based on the cumulative fraction of the original variance accounted for, among other criteria.

For unmixing models in general, samples with a very atypical pattern can distort the analysis, and therefore may be excluded from the dataset before further analyses. (The results can still be applied to any excluded samples to define source contributions, but the fit may be less complete, with somewhat higher residuals [see below].)

In the unmixing analyses for this study, PCA was applied to all 85 sample TEQ profiles to identify outliers. After outliers were removed, a PCA analysis was performed on all remaining samples. Based on the PCA analysis, the number of sources to be included in the unmixing analysis was chosen.

An alternating least squares (ALS) method was then used for the unmixing analysis. The ALS method assumes the dataset reflects the variable contributions from a fixed number of sources. Therefore, the measured values are assumed to be the product of the chemical patterns for the sources and the amounts contributed from each source to each sample. This product is calculated iteratively using matrix algebra, with one matrix of source profiles and a second matrix of source contributions to samples. Starting values are assigned to both matrices to begin the calculations. As the iteration proceeds, constraints are applied; for example, one constraint is that no negative contributions from sources are allowed, because negative contributions lack physical meaning. When the iterative calculations converge, the unmixing model is complete. It provides in its two matrices solutions for the chemical profiles of sources and their contributions to each sample (i.e., sample composition).

The mathematical product of source profiles and fractional contributions for a given sample produces a calculated TEQ component profile for that sample. This calculated profile typically does not match the measured profile exactly. The differences, congener by congener, reflect a "residuals profile" for that sample. The set of residuals across all samples is a measure of the goodness-of-fit of the unmixing model and its ability to reproduce the lab analytical results.

Interpretation of unmixing model results. Subsequent analyses were performed to interpret the unmixing results. Two general questions were of primary interest: (1) are the Port Angeles soil TEQ profiles and the source profiles identified through unmixing analyses similar or dissimilar to other soil dioxin/furan profiles? and (2) can the source profiles identified through unmixing analyses be identified with likely sources in the Port Angeles area?

Numerous additional datasets were compiled to support further evaluations for unmixing model interpretation. In all cases, the available data were processed to provide TEQ component profiles, the same metric used to evaluate study samples. Many comparison datasets were obtained from the published literature or agency reports; some were obtained through personal contacts or internet searches.

Soil dioxin/furan datasets included multiple studies of urban soils, as well as studies of forest and rural/remote soils (Rogowski et al. 1999; EPA Region 8 2001; University of Utah [undated]; Demond et al. 2008; Lubliner 2009; EPA 2007b, 2000; Lorber et al. 1998; Muller et al. 2004; Andersson and Ottesen 2008; Andersson 2009; Schmid et al. 2005; Galli et al. 1992; Van Oostdam and Ward 1995; Bakoglu et al. 2005; Caserini et al. 2004; Broman et al. 1990; Schuhmacher et al. 2004, 1997; Hassanin et al. 2005). A number of previous and recent soils investigations in or near Port Angeles were compiled (E & E 1998a, 1998b, 1999; Landau Associates 2003; Sawyer 2003; Environment International Government 2009; Beckley 2009; Integral 2007). One study of dioxin/furan air deposition in urban areas of Japan was also used (Ogura et al. 2001). Some soil datasets with elevated detection limits and frequent nondetect results, which limited their usefulness for chemical profiling, were identified but not used in the chemometric analyses.

EPA has compiled an inventory of air emission sources for dioxins/furans (USEPA 2006). The inventory is a primary source for calculating TEQ component profiles for a large number of such sources. There is a large and growing body of published literature with additional data on air emissions source profiles. A literature review produced a significant number of source profile references, which provided supplemental information. Ecology's Dioxin Source Assessment report for Washington (Yake et al. 1998) compiled source test data available at that time and provides profiles for recognized state sources (e.g., medical waste incinerators, crematoria). Chemical manufacturing is also recognized for producing incidental dioxins/furans co-occurring with commercial products. Direct application and use of such chemicals can unintentionally introduce dioxins/furans to surface soils. Dioxin/furan profiles for several common chemicals were used as part of the inventory of source profiles (EPA 2000, Burkhard and Lukasewycz 2008, Jiang et al. 1997).

A special effort was made to collect information on source profiles for HFBs burning salt-laden wood. Only a single stack test has been reported for the former Rayonier Mill HFB (FWEC 1997, used by Yake et al. 1998). The congener concentrations were reported as the average of two runs in a single profile and initially used in that manner in the chemometrics evaluations. Data from the two individual runs were located later (AmTest 1995); there was a substantial difference in profile between the two runs, performed successively on the same day[10].

The Canadian government recognized a large concentration of coastal mills in British Columbia, Canada, as a high-ranked source category in its national emissions inventory for dioxins/furans occurring as a result of burning salt-laden wood. Those coastal mills have been subject to intensive study. Through a combination of literature reviews, database queries, and personal contacts, over 60 TEQ component profiles were developed for HFB stack emissions representing multiple British Columbia mills and multiple years of operations (DeAbreu 2009, Glass 2009, Luthe and Prahacs 1993). The Canadian research program produced extensive investigations and models for the formation of dioxins/furans in HFBs burning salt-laden wood and approaches for controlling those emissions (Duo et al. 2002, [undated]; Duo and Leclerc 2007; Duo and Uloth [undated]; Luthe et al. 1994; Luthe and Uloth 1996; Luthe et al. 1997a, 1997b, 1998a, 1998b; Leclerc et al. [undated]; Uloth et al. [undated]; Ulloth and van Heek 2002; Das 2003). In addition to data from large-scale operating facilities, data from several research studies were also located that provided the results of relevant bench-scale testing of the role of salt-laden materials in dioxin/furan formation during combustion (e.g., Yasuhara et al. 2001, 2002, 2003; Katami et al. 2000; Lavric et al. 2004).

The profiles for all these comparative datasets were combined with the profiles for this study's soil samples in Port Angeles to create an expanded dataset. Various screening steps were used to reduce redundancy among the profiles included in the comparative datasets and to focus on the most relevant results through removal of profiles markedly dissimilar to any study samples. Approaches used for evaluating the study data combined with additional datasets included PCA/ALS unmixing analyses, hierarchical cluster analysis (HCA), profile correlation analysis, and target testing (see Appendix C for details). These evaluation approaches focused on examining the relationships between profiles for this study's samples, as originally reported and as determined by the unmixing model results, and a large set of comparison profiles.

Uncertainties. The chemical pattern evaluations are subject to various sources of uncertainty, as is common to all modeling efforts. As previously noted, one common source of uncertainty, chemical patterns compromised by frequent nondetect results, does not substantially affect the Port Angeles soils dataset. Some recognized potential sources of uncertainty are:

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[10] Only one other stack test with dioxin/furan analyses was located for other HFBs in Port Angeles. In 2009, a stack test was conducted for the still-operating Nippon mill located several miles west of the former Rayonier Mill site (AmTest 2009). At the time of this stack test the Nippon HFB was no longer using salt-laden wood; materials had not been received and stored in a marine log pond for many years prior to the test. Dioxin/furan congener profiles for the Nippon 2009 study are included in Appendix D.

- Laboratory analytical issues, such as co-elution of congeners, that affect reported profiles;
- An incomplete source inventory, missing comparison source profiles that are related to study profiles;
- Non-representativeness of source inventory profiles from literature reports or other locations for the site-specific sources of similar type;
- Variability in source profiles over time (e.g., because of changes in facility operations or pollution control systems);
- Changes in profiles between emission sources and receptor media (e.g., soils) due to differential fate and transport processes and weathering effects (losses post-deposition); and
- Highly-correlated impacts from multiple sources that produce composite profiles, affecting comparisons to single source profiles from a source inventory (degraded similarity).

The occurrence of one or more of the factors listed above does not necessarily result in significant uncertainty. For example, a composite profile may still be evaluated by comparison with other profiles that are also composite; many urban soil profiles would be expected to represent multiple sources and composite profiles. Fate and weathering processes that result in some losses compared with emission profiles may in some cases have minimal effects on the usefulness of profile comparisons. A source profile characterized by only furan congeners, for example, may still be diagnostic even with modification to the proportional contributions among furan congeners. In another case, a TEQ component profile with dominant contributions from only lower-chlorinated congeners, which may be affected by fate and weathering processes, may be changed little by losses that are roughly proportional among the dominant (diagnostic) congeners.

For any study, the overall uncertainty associated with chemical pattern evaluations should be assessed in light of identified potential uncertainty factors. The consistency of data interpretations from multiple lines of evidence should also be assessed.

8.3.2 Results

A complete set of TEQ component profiles for the 85 soil samples collected in Port Angeles, grouped by locations, was provided in the Data Summary Technical Memorandum (E & E 2009). Those individual sample profiles are reproduced as Figure 6-10 in this report. The development of these profiles from the data reported by the analytical laboratory, and the distinct changes to the profile shapes, are summarized in three figures[11] (discussed below); each figure is based on a different treatment of the data, but each includes all 85 samples.

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[11] Colors are used to code sample types in these figures: blue = grid, green = forest, red = road, and black = upslope transect. Note that the same colors are also used in other figures to code the three sources identified by unmixing analyses.

Figure 8-6 shows the bulk congener concentration profiles in ng/kg dw. Figure 8-7 shows the calculated TEF-adjusted results for each congener, equivalent to the partial contributions to total TEQ for each congener, in ng TEQ/kg dw. The strong shift in higher peaks from higher- to lower-chlorinated congeners is apparent; the higher-chlorinated congeners are only small contributors to TEQ despite dominating the bulk congener concentrations. Figure 8-8 shows the profiles for each sample after normalization of the profile by dividing each congener value in Figure 8-7 by the total TEQ for that sample, thus making the units for Figure 8-8 scalar values between 0 and 1. After normalization, the sum of the congener fractional contributions equals 1 for each sample.

The profiles in the first two figures are affected by the magnitude as well as by the pattern of congeners in samples; after normalization, the profiles in Figure 8-8 reflect only the pattern, and no longer the magnitude, of congener contributions (i.e., they shift from an absolute to a relative scale). The numerical values for these TEQ-normalized profiles are provided in Table 6-4; the further shift in sample patterns is obvious in Figure 8-8. The profiles as shown in Figure 8-8[12] and listed in Table 6-4 are the basis for the primary chemometric analyses.

The initial PCA analysis identified two outlier samples that were excluded from further unmixing analyses. Sample W209 had the highest total TEQ result of any sample, dominated by the single congener 2,3,7,8-TCDD. Sample E406 had an atypical profile and was identified as an outlier by several outlier diagnostics. Both excluded samples were later evaluated using the unmixing model results based on the remaining 83 samples.

A PCA analysis on 83 samples determined that three factors could account for 99.7% of the dataset variance. Exploratory evaluations were performed for a four-factor model (99.9% of variance), but a three-factor model was deemed satisfactory. The unmixing model was therefore set up for three dioxin sources. Note that the congener loadings that define the PCA factors are not the same as the source profiles for unmixing; a separate analysis was needed to determine source profiles. Figure 8-9 provides the set of two-way PCA factor plots for the three-factor analysis, and shows the spread of the samples in this reduced, three-dimensional space.

The ALS analysis (n = 83) achieved convergence and provided TEQ profiles for three sources and the contribution of each source to each sample. The three source profiles are shown in Figure 8-10. Source 1 (blue) is dominated by very high fractional contribution from 2,3,7,8-TCDD. Source 2 (green) has a dominant contribution from 1,2,3,7,8-PeCDD, large contributions from several other higher-chlorinated dioxin congeners, and a few lower furan peaks. Source 3 (red) also has a dominant peak for 1,2,3,7,8-PeCDD, two elevated furan peaks at 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF, and lower contributions from higher-chlorinated dioxins compared with Source 2.

The contributions of each source to each sample (sample compositions) are listed in Table 8-2. Sample compositions can be shown graphically in two ways.[13] Figure 8-11 provides line plots of

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[12] Figure 8-8 shows all 85 samples in a single plot. Note that the same information is shown as a series of plots for different sample subgroups as Figure 6-10.

[13] The sample index used on the X axis in Figure 8-11 uses the same ordering of samples shown in Table 8-2. Note that because of an initial sample mislabeling in which sample E112 was originally labeled as W112 (there is no

the contributions from each source across all samples (n = 83); Source 3 (red) dominates most samples. Figure 8-12 shows the same data as a ternary plot (3-dimensional, reflecting three sources, shown in 2 dimensions) of sample locations. The clustering of many samples near the Source 3 axis, with most samples on a gradient reflecting a mixing of Sources 2 and 3 and a smaller number of samples with high Source 1 contributions, is seen in this representation of sample compositions.

The unmixing model based on three sources is a good representation of the sample TEQ data, as shown in Figure 8-13 which gives the residual profiles[14] (in scalar values between –1 and 1) for the modeled dataset. The residuals profiles can be compared with the normalized TEQ profiles in Figure 8-8; both figures use comparable Y-axis scaling. The residual values are small.

Several hundred additional TEQ component profiles, from the numerous studies identified in Section 8.3.1, were compiled and used to support interpretation of the three source profiles revealed by the unmixing analysis. The conclusions based on several evaluation methods are briefly summarized here; for details of the evaluations, see Appendix C.

Many of the profiles included in the source inventory of comparison profiles have little or no similarity to the profiles for soil samples from Port Angeles. The urban soil profiles also showed considerable variability, generally greater across studies (i.e., at different locations) than across samples within studies.

Source 1, dominated by the single 2,3,7,8-TCDD congener, has a profile also seen in a number of other urban soil samples. It is most similar to the profiles from tire combustion and the manufactured chemical 2,4,5-T used as an herbicide.[15]

Source 2 is most similar to several urban soil samples, including Port Angeles samples from other studies and Spokane storm drain sediments, and a number of stack test profiles from Canadian HFBs burning salt-laden wood. The relatively high contributions from Source 2 for several samples located near roadways suggest that diesel and/or gasoline fuel emissions may be a significant component for Source 2, at least as part of a composite urban profile reflecting multiple sources. The similarity to a number of HFB profiles from Canadian mills also suggests that the Source 2 profile may be a composite[16] of typical urban soil profiles and a profile from burning of salt-laden wood.

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sample W112), sample E112 appears out of its natural ordering in both the figure and table. Sample E112 is listed between samples W109 and W196.

[14] The unmixing model typically does not reproduce sample TEQ profiles exactly. The difference between the modeled and measured TEQ components, congener by congener, produces the residuals profile for a sample.

[15] A complete dioxin/furan profile for 2,4,5-T was not located and may be considered proprietary information by manufacturers. 2,3,7,8-TCDD is a known dominant congener associated with 2,4,5-T manufacture. Dioxin levels in urban soils could be elevated through direct application of 2,4,5-T. Residential soils near a 2,4,5-T manufacturing facility in Paritutu, New Zealand, have been extensively studied for 2,3,7,8-TCDD contamination (Pattle Delamore Partners Ltd 2002).

[16] In an ideal application, an unmixing analyses would produce source profiles for individual and distinct sources. However, where multiple sources contribute to samples in a positively correlated manner, so that they regularly co-occur in a proportional manner, the “source profile” produced by unmixing may reflect the composite profile of the jointly-occurring source impacts.

Source 3 has strong similarity to a number of other soil samples from Port Angeles (see Integral Consulting, Inc. 2007) and notably to a group of stack emission profiles from Canadian HFBs burning salt-laden wood (DeAbreu 2009, Glass 2009, Luthe and Prahacs 1993). A PCA analysis of the expanded dataset[17] was used to evaluate what other TEQ profiles are most similar to the Source 3 profile from the unmixing analyses. In that PCA analysis, samples that have mostly Source 3 contributions are located close to the single former Rayonier Mill HFB stack test; the large set of Canadian HFB stack test profiles, while presenting minor variability, is clustered at the same location as the former Rayonier Mill HFB stack test and the samples dominated by Source 3. No other sources from the inventory of sources share this pattern as shown by the PCA plot. This is strong evidence supporting the interpretation that Source 3 represents emissions from HFBs burning salt-laden wood.

Unmixing analysis summary. The approach and conclusions for the multivariate evaluations of chemical patterns in the Port Angeles soil samples (unmixing analyses) are summarized as follows:

- Normalized TEQ profiles for the soil samples were developed as the basis for unmixing analyses, which used multivariate PCA and ALS techniques.
- PCA analyses and additional outlier detection methods identified 2 samples with unusual TEQ profiles; unmixing analyses were based on the remaining 83 samples.
- Three sources were determined sufficient to account for almost all (99.7%) of the variance in TEQ profiles across samples.
- The final unmixing model provided distinct TEQ profiles for each of 3 sources.
- The fractional contributions of each source profile to each soil sample were determined by the unmixing analyses, for all 85 samples (including 2 outliers); these results provide a partitioning, or decomposition, of total TEQs for samples into portions contributed by separate source profiles.
- Comparing the unmixing model TEQ profiles to measured TEQ profiles, the differences (residuals, for each congener contributing to TEQ) are small, demonstrating a high degree of goodness-of-fit for the model results.
- Interpretations of the 3 source profiles from unmixing analyses included compilation and review of a large number of characteristic source profiles, among which were numerous stack test results from HFBs burning salt-laden wood.
- Source 1, dominated by a single congener (2,3,7,8-TCDD), is similar to a tire burning profile and the TEQ profile for incidental dioxin formation during 2,4,5-T production.
- Source 2 is similar to a composite urban dioxins TEQ profile, including vehicle emissions; it is also similar to some HFB profiles, and may reflect a composite profile to some degree due to widespread co-occurrence of both typical urban and HFB sources in Port Angeles.

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[17] The expanded dataset combined TEQ profiles for the samples in this study with numerous source profiles and profiles for soils samples from other studies.

- Source 3 has strong similarity to the TEQ profile for stack emissions from a HFB burning salt-laden wood.

8.3.3 Source Increment Magnitudes

The chemometric analysis of the Port Angeles dataset provides a composition for every sample in terms of the fractional contribution from each identified source for each sample (see Table 8-2). The TEQ "increments" from individual sources can be calculated from these results as the product of the fractional contributions and total TEQ. These TEQ values associated by the chemometric modeling with individual sources are referred to here as source increment TEQs, or simply source increments. For a model with three identified sources, each sample TEQ is then seen to be composed of three source increments, and each of the three identified sources has a statistical and spatial distribution of source increments across all 85 samples. Source increments are listed in Table 8-3.

The statistical distribution of total TEQ results is discussed in Section 8.1. The magnitude of dioxins/furans in Port Angeles soils can be revisited in terms of the calculated source increments. Figure 8-14 provides box-and-whisker plots for the numerical distributions of TEQ increments for each of the three sources as well as total sample TEQ values. By inspection of the box-and-whisker plot and associated tabled values by sample, it is apparent that Source 3 increments overall are somewhat higher than increments from Sources 1 or 2. The largest of three source increments can be determined for each of the 85 samples (see Table 8-3); the counts for number of samples with maximum increments by source are 12 for Source 1, 17 for Source 2, and 56 for Source 3.

The contributions of each source increment to total TEQ can also be illustrated using scatter plots in which each of the 85 samples is a separate plotted point. These scatter plots ("part versus whole" figures) have the source increment magnitude on the Y-axis and total sample TEQ on the X-axis; all plotted sample results therefore are on or below the X = Y line. The farther below the X = Y line a plotted sample result falls, the less the selected source increment contributes to total TEQ. Figure 8-15 includes three sets of scatter plots for source increments versus total TEQs, one for each of the three sources from unmixing analyses. Sample types are color-coded in the scatter plots. Two panels are shown for each source increment, the first including all of the 85 results and the second rescaled (omitting 1 or 2 outlier results) to make it easier to see patterns for the bulk of the data set. On each scatter plot reference lines have been added to show where the source increment contributes 25%, 50% or 100% (i.e., the X = Y line) to total sample TEQ.

These scatter plots confirm the information in the box-and-whisker plot (Figure 8-14) regarding the overall relative contributions of the three sources to total TEQ values. Most of the Source 1 contributions are less than 25%, with particularly small contributions to forest and upslope sample types. A subset of grid-type samples with elevated total TEQs, however, is shown to have Source 1 contributions of more than 50% to total TEQ. Source 2 contributions are higher overall, with between 25% and 50% contributions to total TEQ for many samples. Source 2 contributions to forest samples are mostly below 25%; contributions to upslope samples are variable (see Tables 8-2 and 8-3), but at small absolute TEQ values. Most Source 3 contributions are greater than 50%, with particularly high contributions to forest-type samples and the majority of upslope samples. Compared to Source 1 and Source 2, Source 3 has only minor contributions to the two road-type samples.

The chemometric analysis has identified one source, Source 3, as being very similar in profile to emissions from HFBs burning salt-laden wood, with substantial fractional contributions from this source to many samples across the soil dioxins/furans study area. The Source 3 increment can be subtracted from the total TEQ value for each sample. The remaining TEQ values represent the summed contributions from Sources 1 and 2.

The statistical distribution of grid-type sample TEQs is strongly modified by the removal of Source 3 increments. The median TEQ is reduced by almost 60%, from 11.87 to 4.83 ng TEQ/kg. The 75th percentile value is reduced from 17.45 to 8.63 ng TEQ/kg. The box-and-whisker plot of Figure 8-3 comparing grid-type total TEQ results with other urban soils datasets is repeated in Figure 8-16, but with the addition of the Port Angeles dataset with Source 3 increments removed (designated in the figure as PA_NONHFB_GRID). The combined effect from Sources 1 and 2 produces a distribution markedly more similar to other urban datasets, as seen in Figure 8-16 and by comparison of numerical values in Table 8-1. This source increment magnitude evaluation further supports the conclusion that Source 3 produces an atypical enrichment of TEQs in Port Angeles soils.

There are a number of high outlier values for grid-type sample TEQs after removal of Source 3 contributions, as shown in Figure 8-16. Those high outlier results show an interesting pattern. Of the 11 grid-type samples with remaining TEQs greater than 11 ng TEQ/kg (range 15.25 to 76.3 ng TEQ/kg), Source 1 dominates Source 2 in 10 of the 11 samples, with Source 1 contributions of 67.5% to 100% (for 8 of 10 samples, greater than 80%). Source 1 increments for those 10 samples range from 11.18 to 76.3 ng TEQ/kg. The Source 2 increments for those 10 samples are low (range 0.00 to 6.74 ng TEQ/kg,) and within typical urban background soil ranges. The only high outlier residual TEQ with a dominant Source 2 contribution (55.5%; 9.71 ng TEQ/kg Source 2 increment) is for sample W216. Of the 11 high outlier grid-type samples, nine are from the more urbanized western sampling grids and occur in disparate locations. This pattern for the high outlier grid results (absent Source 3 contributions) suggests property-specific rather than area contributions, which is consistent with the interpretation of Source 1 based on chemical patterns as related to tire burning, or, possibly, chemical application of the herbicide 2,4,5-T.

A similar evaluation of forest-type samples with Source 3 increments removed is even more striking. The Source 3 contribution to the 14 forest-type samples is notably high, exceeding 70% for 11 of the 14 samples. After removal of Source 3 increments, 12 of the 14 forest-type samples have remaining TEQs of only 0.85 to 3.93 ng TEQ/kg. The Washington state survey (n = 8) had median and 75th percentile TEQs of 3.49 and 5.60 ng TEQ/kg, respectively (see Table 8-1) using one-half the higher detection limit for nondetect results, even though the sampled locations were not on the urban fringe. (Although the sample sizes were small, forest TEQs were generally somewhat higher in the western versus the eastern part of the state.) The remaining two forest-type samples from Port Angeles are interesting with respect to their locations. Sample FF01 had a TEQ of 8.96 ng TEQ/kg (absent the Source 3 increment); almost all of this (8.22 ng TEQ/kg) was associated with Source 2. Source 2 is associated at least in part with road/vehicle emissions; FF01 is located adjacent to Highway 101, the most heavily traveled road in the area. Sample E403 was collected just north of the Mt. Pleasant landfill, where heavy equipment operations occurred. The remaining TEQ after removal of the Source 3 increment was 23.6 ng TEQ/kg, of which 20.71 ng TEQ/kg was associated with Source 2. The evaluation of source increment magnitudes for forest soils also supports the conclusion that Source 3 produces atypical TEQ enrichment.

Showing total TEQs and the contributions of Source 3 to total TEQs together in a single map also illustrates the importance of Source 3 to the unmixing model results, in particular for locations exceeding the MTCA Method B value. In Figure 8-17, all samples with total TEQ greater than 11 ng TEQ/kg are designated with a colored symbol; locations with less than 11 ng TEQ/kg are shown with an open symbol. Source 3 contributions to samples with greater than 11 ng TEQ/kg are indicated by an intensity scale for the ranges of less than 4 ng TEQ/kg, between 4 and 11 ng TEQ/kg, and greater than 11 ng TEQ/kg. Note that Source 3 contributions to locations shown with an open symbol (total TEQ less than 11 ng TEQ/kg) for the most part are not zero (Table 8-3), but those contributions are not shown in Figure 8-17.

The relative contributions of the three unmixing sources to total TEQs exceeding 11 ng TEQ/kg can also be examined by omitting the contributions of one source type at a time. For the full data set of 85 samples, including all sample types, there are 40 samples with total TEQs greater than 11 ng TEQ/kg. If all Source 1 increments are omitted, the number of sample locations exceeding 11 ng TEQ/kg drops to 25. As noted above and shown in Figure 8-15, a subset of grid-type samples has notably high Source 1 increments. Among the 15 samples with the highest total TEQ results (greater than 20 ng TEQ/kg), Source 1 alone contributes approximately 50% or more of total TEQ and more than 11 ng TEQ/kg to nine locations. If all Source 2 increments are omitted, the number of sample locations exceeding 11 ng TEQ/kg drops to 27, almost the same as if Source 1 increments are omitted. Source 2, however, has only a single location (a forest-type sample) with a TEQ increment above 11 ng TEQ/kg. The influence of these two sources on the number of sample locations exceeding 11 ng TEQ/kg is thus similar in magnitude, but arises from different patterns: Source 1 has mostly small TEQ increments, but has a subset of much higher values, while Source 2 has only a single higher-tier result but many samples with mid-range TEQ increments. If all Source 3 increments are omitted, the number of sample locations exceeding 11 ng TEQ/kg drops to 12. While only 13 samples have Source 3 increments above 11 ng TEQ/kg, only marginally more than the ten samples with Source 1 increments above 11 ng TEQ/kg, the remaining Source 3 increments are overall much higher than Source 1 increments. The influence of Source 3 on the number of sample locations exceeding 11 ng TEQ/kg thus arises from both individual increments above 11 ng TEQ/kg and substantial contributions to many other samples at magnitudes somewhat below 11 ng TEQ/kg (see Table 8-3 and Figure 8-15). Measured by the number of remaining sample locations with TEQs above 11 ng TEQ/kg after removing the influence of an individual unmixing source type, Source 3 is demonstrated to have the largest overall effect across the entire study area and all sample types.

Source increment magnitude summary. The approach and conclusions for the evaluation of source increments for Port Angeles soil samples are summarized as follows:

- The unmixing model results were used to calculate TEQ increments from each of three source profiles for each of the 85 soil samples.

- Source 3 has a large contribution to total TEQ for many of the sampled locations; for grid-type samples, subtracting the Source 3 increments reduces the median TEQ by almost 60%.
- After subtracting Source 3 increments for grid-type samples, the remaining sample TEQs (sum of contributions from Sources 1 and 2) are similar to total TEQ results from other studies of urban soils; including Source 3 increments, the distribution of grid-type samples appears shifted higher compared to other studies of urban soils.
- After subtracting Source 3 increments for grid-type samples, remaining TEQs greater than 11 ng TEQ/kg are dominated by Source 1 contributions (10 of 11 cases); all Source 2 increments for grid-type samples are less than 9.7 ng TEQ/kg, with 47 out of 60 (78%) less than 5 ng TEQ/kg.
- Source 3 dominates most forest-type samples (greater than 70% contribution for 11 of 14 samples). After subtracting Source 3 increments, 12 of 14 forest-type samples have remaining TEQs less than 4 ng TEQ/kg, comparable to or lower than the TEQs for forest-type samples in the Washington statewide survey (Rogowski et al. 1999). The two higher remaining TEQs (8.96 and 23.6 ng TEQ/kg) are dominated by Source 2 contributions and are located near a major roadway and a landfill with heavy equipment operations.
- Source 3 has only minor contributions to two roadside-type samples collected outside of heavily developed areas of Port Angeles.
- Source 3 has large contributions to many of the upslope transect-type samples (57% to 81% for 6 of 9 samples), although Source 3 increments and total TEQs are low. This result was not anticipated as part of the Conceptual Site Model.
- Source 3 has the largest influence on the number of sample locations exceeding 11 ng TEQ/kg. Of the 40 samples out of 85 total locations that have total TEQs above 11 ng TEQ/kg, the number remaining if individual unmixing source increments are omitted is 25 without Source 1, 27 without Source 2, and only 12 without Source 3.
- Among the 15 samples with the highest total TEQ results (greater than 20 ng TEQ/kg), Source 1 alone contributes approximately 50% or more of total TEQ and more than 11 ng TEQ/kg to nine locations. Source 1 thus has the major influence on a subset of the samples with highest total TEQ results.

8.3.4 Source Increment Spatial Patterns

The unmixing analysis of the Port Angeles dataset supports a more focused and useful evaluation of spatial patterns than an analysis based on total TEQ results (Section 8.2). The contributions to each sample from individual sources (source increments) identified by the unmixing modeling can be shown in spatial maps. Spatial mapping of the TEQ increments from individual sources illustrates the scale of impact of the separate sources and thereby provides more detailed information than mapping using total TEQs before unmixing, as discussed in Section 8.2.

A spatial map of total TEQ results for all samples coded by sample type is provided in Figure 8-5. In a similar manner, using the source increments determined from the unmixing model, two-dimensional spatial dot maps were prepared for TEQ increments from Source 1, Source 2, Source 3, and Sources 1 plus 2 and are presented as Figures 8-18, 8-19, 8-20, and 8-21, respectively. Most grid-type samples were collected from residential lawns; a few were collected from open fields.

Source 3, with a chemical profile similar to emissions from HFBs burning salt-laden wood, was shown to have relatively large fractional contributions to most of the Port Angeles samples (Table 8-2). The dominance of contributions from Source 3 is especially notable for the eastern sampling zones. Considering the combined 74 samples that are either grid- or forest-type (omitting two roadside-type samples and nine upslope transect-type samples), Source 3 contributions of at least 40% occur for 38 (92.7%) of 41 eastern samples and 17 (51.5%) of 33 western samples. Source 3 has the highest TEQ increment of the three sources for 34 of 41 samples in the east zones and for 16 of 33 western samples. This pattern is consistent with the dominant wind direction and likely also reflects additional contributions from other sources in the more developed western portion of the soil dioxins/furans study area.

Spatial mapping based on calculated source increments using the unmixing model results offers the most direct approach to determining absolute rather than relative impacts and contributions from individual source profiles over the soil dioxins/furans study area.

The mapping of Source 3 increments in Figure 8-20 shows a strong spatial pattern for grid samples, with clusters of high-TEQ increment values close to the former Rayonier Mill HFB stack, and an inverse distance relationship. The areas of greatest Source 3 increments occur just southeast and southwest of the former stack location. The 10 highest Source 3 increments for grid samples range from 10.22 to 19.31 ng TEQ/kg and all occur in sampling zones E1 (Gale's Addition) or W1, or adjacent to those zones (samples E201 and W204). An additional 15 grid-type samples have Source 3 increments between 5 and 10 ng TEQ/kg, and also occur primarily in sampling zones E1 and W1 (Table 8-3). The cluster of high Source 3 increments to the southeast is generally downwind of the HFB stack according to available wind roses (see Section 3.1). The cluster to the southwest is not in a dominant downwind direction based on available wind roses. The proximity of this cluster to the Rayonier HFB, uncertainty about the applicability of off-site wind roses, observations of the Rayonier HFB plume behavior (Werner 2010), and the distance to other Port Angeles potential dioxin sources with a Source 3 (HFB) profile are factors to consider in evaluating any connection between this southwest cluster and Rayonier emissions. A medical waste incinerator formerly operated at Olympic Memorial Hospital, co-located with the cluster of higher Source 3 increments southwest of the former Rayonier Mill HFB stack (see Figure 4-1). No stack test results or facility-specific TEQ profiles are available for that medical waste incinerator. TEQ profiles for other Washington State medical waste incinerators, however, are not similar to the Source 3 profile from unmixing analyses (see Appendix D).

Additional higher Source 3 increments occur at the far western end of the soil dioxins/furan study area. There are other potential dioxin/furan emissions sources likely to have, or that have had, a TEQ profile like Source 3 (HFB) located to the west of the area sampled for this study (see Section 8.4 and Figure 2-1). With available wind rose data, these additional higher Source 3 increment locations would be largely downwind of the other potential sources and upwind of the

Rayonier Mill. As distances from the former Rayonier mill increase to the west, higher contributions from other HFBs are more likely.

In contrast to Source 3 increments, the dot maps for Source 1 and Source 2 increments do not show strong spatial patterning. The Source 1 increment map shows widely distributed "hot spots," consistent with property-specific sources of dioxins/furans. All of the higher Source 1 increments are at grid (residential) sampling locations; none occur at relatively less developed road, forest, or upslope locations. As noted above, Source 1 has the largest contribution to a subset of samples with the highest TEQ values. The majority of Source 1 increments are small, with 43 of 60 grid locations (72%) being less than 3 ng TEQ/kg. Source 2 increments show a relatively even spatial pattern, also with the majority of locations having small TEQ increments (47 of 60 grid locations [78%] less than 5 ng TEQ/kg). Other than two forest locations, the road, forest, and grid sampling locations have small Source 2 increments. As already noted, Source 2 increments compare favorably in magnitude with typical urban soil TEQs as reported in a number of other studies. The combined Source 1 plus Source 2 increment map has marginally higher TEQs than either source separately, while retaining the "hot spots" due to Source 1 increments (see Figure 8-21).

The 14 forest-type samples are shown as triangle symbols in Figures 8-18 through 8-21. Because of the limited occurrence of forested areas, all forest-type samples are located in the eastern part of the soil dioxins/furans study area at some distance from the Rayonier mill, except for sample W299, taken from along upper Lauridsen Boulevard. The total TEQ results for the 14 forest-type samples ranged from 4.02 to 40.46 ng TEQ/kg, with sample W299 at 12.04 ng TEQ/kg. All but one of the forest-type samples had a Source 3 fractional contribution of more than 67%, with 10 at more than 75% (Table 8-2). The single exception, sample E403 (collected just north of the Mt. Pleasant landfill), also had a substantial Source 2 contribution (20.55 ng TEQ/kg) that reduced the (relative) Source 3 contribution. That sample still had a large Source 3 increment of 16.98 ng TEQ/kg.

The density of grid-type samples located near forest-type samples is not high, but relatively co-located grid-type samples can be compared with forest-type samples. Sample W299 can be compared with nearby samples W208, W211, and W212. Most of the forest-type samples in the eastern soil dioxins/furans study area can be compared with samples E204, E208, E298, E405, E406, and E499. The forest-type samples have comparatively higher total TEQs and higher Source 3 fractional contributions. Source 3 increments for eight of the nine comparison grid-type sample locations are less than 5 ng TEQ/kg, but greater than that value for 12 of the 14 forest-type sample locations. Source 3 is still the highest contributor among the three sources for seven of the nine comparison locations, despite lower Source 3 increment values. Subtracting Source 3 increments from both forest-type and relatively co-located grid-type samples produces comparable residual TEQ values (Source 1 plus Source 2 increments; see Table 8-3 and Figure 8-21). The generally higher total TEQs at forest-type sampling locations thus are largely the result of increased Source 3 increments.

The nine upslope transect-type samples had low total TEQs, with a range of 0.80 to 2.39 ng TEQ/kg for eight locations plus one high outlier of 5.54 ng TEQ/kg. Source 3 fractional contributions for six of the nine upslope samples were high, from 56.8% to 81.0%. Source 2 dominated for three samples; Source 1 had very low contribution to any upslope sample. Field notes confirm that the sample with the highest Source 2 contribution (T104, at 85.6% and a total TEQ of only 2.39 ng TEQ/kg) was collected adjacent to a road. The high Source 2 contribution is thus consistent with the interpretation of Source 2 based on chemical profiles. The low total TEQs for upslope locations are consistent with the conceptual model that was used to develop the sampling design; the frequent high contribution of Source 3, interpreted to be related to HFB emissions, was not expected.

A contouring program was used to develop a contour map for Source 3 TEQ increments at grid-type sampling locations; the results are shown in Figure 8-22. Restricting this contour map to a single sample type avoids the potential for confounding that is associated with combining multiple sample types. Contours showing Source 3 TEQ increment trends were interpolated using the results of 60 grid-type sample locations. The interpolation was carried out in ArcGIS (2010). The interpolation method used to create the contours was Natural Neighbors, which uses an area-weighted subset of points around each grid-type sample location to interpolate values. This method was first used to produce raster surfaces with a cell size of 50 feet. Then the Contour function was used to convert the raster surfaces to the contours shown in Figure 8-22. For reference, sample location codes are shown in Figures 4-1 through 4-8, and actual total TEQ values are mapped in Figures 6-3 and 6-4.

The contour map of Source 3 increments may help to visualize the modeled spatial patterns for contributions to TEQ from a source or sources similar to HFB emissions. Note that this contour mapping cannot be used to predict values at unsampled locations. Local variability in soil dioxin/furan concentrations may be high and is likely to reflect individual property histories.

Spatial mapping of TEQ increments allows spatial trends to be examined for source increments as well as total TEQ. Scatter plots of grid-type (n=60) and upslope (n=9) samples, showing distance from the former Rayonier HFB stack versus TEQ (total or source increment) are provided in Figure 8-23. Other than separating east zone and west zone samples, these generalized scatter plots do not take direction into account; samples at a given distance on the plot may represent a range of directions from the HFB stack. West-zone samples are assigned negative distances by convention for plotting purposes. Upslope samples are shown on the east side of the distance scale.

All 69 grid and upslope sample results are included in the four panels on the left side of Figure 8-23. From the top down, the four panels show distance versus TEQ for total TEQ, Source 1 increment, Source 2 increment, and Source 3 increment. The four panels on the right side of Figure 8-23 include only east zone and upslope results (n=37) at an expanded scale[18] to better show patterns. All of the west zone sampling locations are considered urban. East zone samples extend from the eastern margin of heavily developed residential areas of Port Angeles, including the Gale’s Addition neighborhood, to more rural areas to the east (see Figure 3-3). Upslope sampling locations reflect the least developed portion of the area studied. The number of sampling locations decreases at greater distances.

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[18] In addition to an expanded distance scale on the X-axis, note that the vertical TEQ scale has changed in the two upper right-hand panels.

Spatial trends and gradients from the most developed to the least developed sampling areas are best demonstrated by the scatter plots on the right side of Figure 8-23. Total TEQ versus distance results (top panel) show an apparent decreasing trend with distance, with one high outlier result at a distance of about 15,000 feet (sample E499, dominated by Source 1 contribution). An exponential model for regression on distance is statistically highly significant (model: TEQ = exp(2.78 – 0.000106*DISTANCE); R-squared = 47%; p<0.0001; n=37). Source 1 increment versus distance (second panel) does not show much in the way of spatial trend, but both Source 2 increment and Source 3 increment show an apparent exponential decrease with increasing distance. Exponential models for regression on distance are statistically highly significant for both Source 2 increment and Source 3 increment (in the latter case, whether one Source 3 increment value of 0 is omitted or assigned a small surrogate value to allow exponential regression modeling). The Source 2 regression model is Source 2 increment = exp(1.62 – 0.00012*DISTANCE) (R-squared = 57%; p<0.0001; n=37). The Source 3 regression model (omitting sample E299 with a Source 3 increment of 0) is Source 3 increment = exp(2.32 – 0.00013*DISTANCE) (R-squared = 45%; p<0.0001; n=36).

The scatter plots including all 60 grid samples, on the left side of Figure 8-23, expand these results by adding more urban land use sampling locations. Higher Source 1 increments are seen to be more common in the more developed portions of the study area (panel two on the left of Figure 8-23). The highest single TEQ result (76.3 ng TEQ/kg) is seen to be an outlier for both total TEQ and Source 1 increment. In general, total TEQ, Source 2 increments, and Source 3 increments are seen to be similar in magnitude and range for the most developed part of the east zone plus upslope scatter plots (smallest distances on right panel scatter plots) and across the urban core of Port Angeles (left panel scatter plots). The west zone Source 3 increments include both the cluster of higher values near to and southwest of the former Rayonier Mill HFB stack and the three higher values (8.19 to 9.73 ng TEQ/kg) at the far western portion of the study area, discussed above.

Source increment spatial pattern summary. The approach and conclusions for the evaluation of spatial patterns for the source increments determined by unmixing analyses are summarized as follows:

- Two-dimensional spatial mapping of soil total TEQ results was refined using source increment results from unmixing analyses.
- Concentration maps ("dot maps") for all samples coded by sample type were prepared for each of three separate source increment datasets, to evaluate patterns related to specific source profiles. A contour plot (using the Nearest Neighbor contouring technique) was also developed for Source 3 TEQ increments to further illustrate spatial patterns for those source increments.
- Source 1 increments show widely distributed, isolated "hot spots," consistent with property-specific dioxin/furan sources (e.g., tire burning or possibly chemical application of the herbicide 2,4,5-T), with most values (43 of 60 grid locations, or 72%) less than 3 ng TEQ/kg. Source 1 increments at all forest, road, and upslope sampling locations are small.

- Source 2 increments show a relatively even spatial distribution with many low concentrations (47 of 60 grid locations, or 78%, less than 5 ng TEQ/kg) and a small number of higher outlier values up to 9.7 ng TEQ/kg. Of all road, forest, and upslope sampling locations, only two forest sampling locations have higher outlier values for Source 2 increments.
- In contrast to Sources 1 and 2, Source 3 increments show strong spatial patterning with clusters of high values close to the former Rayonier Mill HFB stack, with 26 of 60 (43%) grid locations greater than 5 ng TEQ/kg and 10 of 60 (17%) greater than 10 ng TEQ/kg. Road and upslope Source 3 increments are small; forest sampling locations have comparatively elevated Source 3 increments, with 6 of 14 locations above 10 ng TEQ/kg.
- One cluster southeast of the former Rayonier Mill HFB stack (in the Gale’s Addition area) is proximate to and generally downwind of the HFB location.
- A second cluster southwest of the former Rayonier Mill HFB stack is proximate to the HFB location, but not in a dominant downwind direction according to the wind roses from Ediz Hook. The representativeness of those off-site wind roses is uncertain. The spatial pattern and proximity of these elevated Source 3 increments to the southwest, as well as observations of Rayonier HFB stack plume behavior and the distance to other Port Angeles HFBs assumed to have similar Source 3 profiles, are factors to consider in evaluating any connection between this southwest cluster and the Rayonier HFB. A former medical waste incinerator co-located with the southwest cluster has no stack test data, but the TEQ profile for this type of source is not similar to the Source 3 profile.
- Beyond the proximate areas of higher Source 3 increments, values at grid sampling locations fall off substantially to the east and the south.
- Several higher Source 3 increments occur at the far western end of the soil dioxins/furans study area, closer to other potential HFB sources in Port Angeles. With available wind rose data, these additional higher Source 3 increment locations would be largely downwind of the other potential HFB sources and upwind of the Rayonier Mill. As distances to the west from the former Rayonier mill increase, higher contributions from other HFBs are more likely.
- Source 3 increments contribute more than 40% to total TEQ concentrations for 38 of 41 (93%) grid- and forest-type samples in the eastern sampling zones, and 17 of 33 (52%) in western sampling zones. Source 3 has the highest TEQ increment of the three sources for 34 of 41 samples in the east zones, and for 16 of 33 western samples.
- The inverse distance relationship from the Rayonier HFB location for Source 3 increments, with a Source 3 TEQ profile similar to emissions from HFBs burning salt-laden wood, provides evidence that those HFB stack emissions have impacted off-property soils. Source 3 increments generally decrease, but not to zero, as distance from the Rayonier HFB increases (both upwind and downwind). In addition to the Rayonier HFB, other Port Angeles sources with a similar TEQ profile may contribute to Source 3 TEQ increments as mapped.

- Urban-to-rural gradients in total TEQs, Source 2 increments, and Source 3 increments, but not Source 1 increments, are shown in distance versus TEQ concentrations for east zone plus upslope samples.

8.4 Mass Balance/Source Emissions

Mass balance analyses are another way to support interpretation of sources, independent of magnitude, spatial patterns, and chemical patterns. Calculation of source increments from chemometric analyses, combined with spatial mapping of those source increments, can be used to estimate the total source-related mass (in TEQ) for a single source profile within the study area soils for the depth interval sampled. To be credibly identified with a chemometric-profiled source, an area dioxin emissions source or sources should be able to account for the calculated source-related mass in study area soils, taking into account that only a fraction of emitted dioxins are deposited locally.

Mass balance analyses are based on a comparison of estimated cumulative air emissions of dioxins and estimated soil dioxins. Consistent with other source evaluations in this study, the mass balance analysis is based on TEQ mass and addresses Source 3 TEQ increments. Estimates of air emissions based on extensive direct stack tests are preferred but are rarely available; absent direct measurements, indirect estimates must be used. Estimates of soil TEQ mass are subject to sampling errors, given the limited number of soils analyzed; they also do not include any TEQ mass for soils at depths below those sampled (0 to 3 inches in this study), nor do they account for potential post-deposition losses of dioxins from soils[19]. A fractional deposition of dioxins to study area soils must also be assumed. Given the limited data available and the number of assumptions required to complete a Source 3 TEQ increments mass balance, the evaluations provided here are considered exploratory.

Soil TEQ mass estimate. Source 3 increments are available for all samples (see Table 8-3). The study design produced variable sample densities across the study area; therefore, a simple averaging of the Source 3 increments might produce a biased estimate of the average Source 3 increment. For the purposes of this mass balance, an area-weighted average was calculated based on stratification of the study area using the sample design sampling zones. (More sophisticated spatial averaging calculations using Thiessen polygons, inverse distance weighting functions, or kriging are not required; their potential greater precision, given the available dataset, is deemed more apparent than real.) The sampling design was based on a constant grid size within each sampling zone; deviations from this arrangement based on access agreements and other factors were relatively minor.

An area-weighted average Source 3 increment was calculated using the results from 70 of the 85 study samples. Details of the approach included the following:

- All upslope transect-type samples and roadside-type samples were omitted

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[19] Ignoring any TEQ mass below 3 inches and any potential post-deposition losses both bias the estimated mass deposited from air emissions low; sampling errors may contribute to either high or low estimates.

- With certain exceptions as noted below, both grid- and forest-type samples were included (assuming the limited number of forest-type samples was representative of and proportional to forested portions of the sampling zones)
- Sampling zone E3, which had only a single sampling location, was omitted
- The sizes of the six remaining sampling zones (W1, W2, W3, E1, E2, and E4) were obtained from the Soil Sampling Plan, Table 5-1 (E & E 2008; see also Table 3-1 in this report)
- In addition to the nine upslope transect-type samples, two roadside-type samples, and one zone E3 sample (E302), three additional sample results were excluded: E199, located in a ravine between zones W1 and E1 and potentially unrepresentative of upland soils; E402, located south of the study area; and E403, located near the Mt. Pleasant landfill and potentially anomalous.

For each of the six zones, the Source 3 increment results from applicable samples were averaged. The results by zone were as follows:

- Zone W1: 0.25 square miles, n = 10, average 7.03 ng TEQ/kg
- Zone W2: 0.93 square miles, n = 17, average 3.86 ng TEQ/kg
- Zone W3: 0.80 square miles, n = 6, average 6.12 ng TEQ/kg
- Zone E1: 0.32 square miles, n = 18, average 7.52 ng TEQ/kg
- Zone E2: 0.86 square miles, n = 11, average 9.73 ng TEQ/kg
- Zone E4: 0.76 square miles, n = 8, average 6.70 ng TEQ/kg

The relatively elevated forest-type sample TEQs primarily affected the calculated averages for zones E2 and E4.

From these results by zone, an area-weighted overall average Source 3 increment was calculated to be approximately 6.7 ng TEQ/kg for the 3.92 square miles included. Total estimated mass of dioxins/furans (as Source 3 TEQ) in the sampled soils was calculated using the following factors:

- The area-weighted average Source 3 increment (6.7 ng TEQ/kg = 6.7 ppt)
- The total study area included (3.92 square miles)
- The sampled depth interval of 0 to 3 inches gives a length of 0.25 feet
- Soil mass (90 pounds/cubic foot, dry weight basis)
- Units conversion factors (1 sq. mile = 5,280 x 5,280 sq. feet; 1 pound = 454 grams)

The resulting estimate of the Source 3–related mass of dioxins/furans in study area soils (0 to 3 inches) is approximately 7.5 grams TEQ. This estimate is subject to several uncertainty factors, as noted above. The calculation also does not take into account the possible composite nature of chemometric profiles, for example any HFB-related component within Source 2 (see Appendix C). The effects of composite profiles are believed to be relatively small and likely biased toward under- rather than over-estimating a Source 3 TEQ mass in area soils. Activities that disturb surficial soils in developed residential areas through mixing/dilution or physical removal are likely to reduce measured soil dioxin/furan TEQs compared to what they would have been in undisturbed soils (for example, Gales Addition in sampling zone E1).. Using recent soil measurements from developed areas may thereby result in estimates of total historical deposition that are biased low.

The estimate of 7.5 grams TEQ is clearly a lower bound value for cumulative source emissions because the fractional deposition within the study area would be far less than 100% (Lohman and Seigneur 2001, whose modeling studies indicate that 80 to 90% or more of air emissions of dioxins typically are transported significant distances downwind). For fractional deposition of 10% to 20% or less, a factor of 5 to 10 times or more would apply to the direct mass calculation for estimating total source emissions. The resulting estimate of cumulative source emissions would thus be in the tens of grams TEQ.

Estimates of cumulative emissions from potential Port Angeles area sources are needed to compare against the mass estimate developed from soils data. Direct measurements of emissions are largely lacking, a typical scenario especially considering decades-long periods of operations at some facilities. Available information is used to derive representative (order-of-magnitude) estimates. In the following sections, air emissions estimates are developed for the former Rayonier Mill HFB, other Port Angeles HFBs that historically burned salt-laden wood, residential wood burning throughout Port Angeles, and the Port Angeles medical waste incinerator. The first three are area sources that are or may have been consistent with a Source 3 TEQ profile from unmixing analyses, and the fourth is nearly co-located with the former Rayonier Mill HFB.

Former Rayonier Mill air emissions estimate. HFB stack dioxin/furan emissions at the Rayonier Mill were measured once in 1995 through a stack test performed in two successive runs in April (AmTest 1995). The average 2,3,7,8-congener profile for the two runs was reported by FWEC (1997) in its summary of site information. That average profile was then used by Ecology (Yake et al. 1998) to calculate daily HFB dioxin/furan emissions as mg TEQ/day. The resulting estimate was 0.17 mg TEQ/day. Three features affect the calculation: (1) older TEF values were used; (2) the summary estimate is based on ND = 0 assignments for nondetect congeners (although the detailed appendix calculations in Yake et al. 1998 include all three standard substitution rules for NDs); and (3) there are significant differences between the two runs, with frequent nondetect congener concentrations in one run, and inconsistent development of average concentrations (see FWEC 1997) for cases where only one of the two runs had a nondetect result. The data for both runs are available in the original AmTest report (1995). Recalculations for the two runs separately, using Ecology’s current TEFs and ND = 1/2 DL assignments for nondetect results, were performed. The average daily HFB stack emissions based on these recalculations were 0.079 ng/m3, equivalent to 0.21 mg TEQ/day or 0.077 grams TEQ/year.

The Rayonier mill operated from 1930 to 1997 (FWEC 1997). If the calculated HFB emission rate of 0.077 grams TEQ/year is applied linearly to the 67 years of operations, the cumulative emissions would be about 5.2 grams TEQ dioxins/furans. However, emissions were reduced over the years of operation as improvements were made. The FWEC rep.ort provides a summary of operational history and includes the following notes (FWEC 1997, page 2-2, verbatim):

- 1974: Waste wood boiler and scrubber replaced to increase boiler capacity and reduce particulate emissions
- 1981: Waste wood boiler scrubber was again upgraded

The degree of improved control on the HFB is indicated by the reduction in particulate emissions when an electroscrubber was installed. The Uplands Remedial Investigation deposition modeling report (Integral Consulting 2007, Appendix H, Table 1) notes a reduction from 327.5 to 19.9 lb/hr in particulate emissions, or more than 16-fold. While particulate emissions are an imperfect indicator for dioxin/furan emissions, this large reduction nevertheless suggests that HFB stack emission were likely much higher for the initial decades of mill operations. As an illustrative calculation, if TEQ emissions were 10 times higher for the first 40 years of operation, the cumulative emissions would be (40 yrs x 0.077 g TEQ/yr x 10) + (27 yrs x 0.077 g TEQ/yr) = 30.8 g TEQ + 2.1 g TEQ = 32.9 g TEQ. The HFB stack emissions from the Rayonier Mill thus appear to be a credible source for cumulative dioxin/furan emissions on the order of tens of grams TEQ, generally consistent with the requirement based on calculations from soil measurements.

Comparative Canadian HFB air emissions. Dioxin/furan emissions estimates are available for a number of other facilities burning salt-laden wood, particularly for Canadian coastal facilities (in British Columbia), which cumulatively were one of the highest ranking sources for the Canadian national inventory of air emissions of dioxins. The available data reflect measurements collected over the past 10 to 15 years, and therefore do not reflect earlier periods when control systems and boiler designs were likely less effective in reducing emissions. Reported emission values varied by facility, as well as over repeated measurements over time within a facility, with an overall downward trend over time as additional controls were implemented. Many of the annual emissions estimates were in the range of a few tenths of a gram TEQ per year to over 1 g TEQ/yr; the calculated 1995 value of 0.077 g TEQ/yr for the Rayonier Mill given above is at the low end of the range of compiled literature values from Canadian coastal mills[20]. The large number of emissions measurements from similar facilities puts the single Rayonier Mill stack test in context and supports the order-of-magnitude calculations for Rayonier emissions (see, among other references, the following: Canadian Council of Ministers of Environment 2004, Luthe et al. 1996, Luthe et al. 1997a, Luthe et al. 1998, DeAbreu 2009 and the Canadian NPRI website, Lavric et al. 2004, Yasuhara et al. 2003, Preto et al. 2005, Duo and Leclerc 2007, Duo and Uloth [undated], Uloth et al. [undated], Duo et al. [undated], Leclerc et al. [undated], Glass 2009).

Other Port Angeles HFBs. For other dioxin sources where salt-laden wood was burned in HFBs in Port Angeles, only one other stack test for dioxin air emissions was located. In 2009, a stack test was performed for the Daishowa (Nippon) mill (AmTest Air Quality 2009). That stack test included three separate runs. TEQ concentrations were calculated for each run, using ½ DL for ND results, from reported results expressed as pounds per hour for each of 17 2,3,7,8-congeners. Total TEQs ranged from 0.6214 to 1.1179 x 10^{-9} pounds TEQ per hour, with an average value of 0.8239 x 10^{-9} pounds TEQ per hour. Assuming continuous operation throughout the year, this is equivalent to 0.0033 grams TEQ/year air emissions. The estimated HFB emissions from the former Rayonier Mill based on the 1995 stack test, 0.077 grams TEQ/year, are more than 23 times greater than the estimate of 0.0033 grams TEQ/year calculated from the 2009 Nippon HFB stack test. At the time of the 2009 stack test, and for many years prior, the Nippon mill was not

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[20] Increasing the annual emissions calculated from the 1995 stack test at the former Rayonier Mill HFB by a factor of 10, as in the illustrative calculation above, would result in annual dioxin emissions still well within the range reported for the Canadian coastal mills within the last 10 to 15 years.

burning salt-laden wood; delivery of materials by water and storage of logs in a marine log pond was standard during earlier mill operations. The comparison of estimated annual TEQ emissions from the Nippon and former Rayonier mills, with substantially higher emissions associated with burning salt-laden wood versus non-salt-laden wood, is consistent with literature reports associating salt-laden wood with higher emissions (see Das 2003, Pandompatam et al. 1997, Luthe and Prahacs 1993, Duo et al. [undated], Duo and Leclerc 2007, EPA 2006, Van Oostdam and Ward 1995). The TEQ profile for the 2009 Nippon mill HFB stack tests is generally similar to the profiles for HFBs burning salt-laden wood, including the former Rayonier mill (see Appendix D).

Data are also available for boiler ash dioxins for the Nippon and former Rayonier mills, presenting the same type of comparison between burning non-salt-laden wood and salt-laden wood. Yake et al. (1998) provide estimated loadings from boiler ash for both mills. The result for Rayonier (22.2 mg TEQ/day) is 1,850 times greater than the value for Daishowa (0.012 mg TEQ/day). Daishowa HFB ash was disposed of at a Port Angeles-area landfill (Lawson Landfill) starting in 1983, reportedly well after use of the marine log pond ended. Deep cores in the ash disposal area were collected and tested for dioxins/furans in 1998 (E & E 1998d). The TEQs for six ash samples ranging up to 17 feet below the surface were from 0.48 to 1.6 ng TEQ/kg. In contrast, results for Rayonier ash at times exceeded 10,000 ng TEQ/kg (FWEC 1997; see also E & E 1998b and 1998c for results of sampling at Rayonier ash disposal landfills). Both HFB ash and air emissions data thus confirm that burning salt-laden wood can substantially increase dioxin levels.

The potential dioxin air emissions from other Port Angeles HFBs associated with burning salt-laden wood, and not recent periods of burning non-salt-laden wood, are of greatest interest for the mass balance analysis. Historically, the operations of several other facilities, including the Daishowa (Nippon) mill, K-Ply (formerly Pen-Ply), and Fibreboard plant (see Figure 2-1), involved marine delivery and storage of materials and therefore burning of salt-laden wood wastes (see Yake et al. 1998, Martin 1983, and Plywood Pioneers Association 2001). There are no direct measurements of air emissions from those facilities from which to derive dioxin mass emissions. Cumulative dioxin emissions from these facilities would reflect the duration of operations, the annual amounts of salt-laden wood burned, boiler and pollution control system designs, and other factors. Given the size and operating histories of these other Port Angeles locations with HFBs, their combined (and in some cases individual) cumulative over time dioxin/furan TEQ air emissions may well have totaled tens of grams TEQ (order-of-magnitude), similar in scale to the estimated cumulative emissions from the former Rayonier Mill.

The Source 3 profile from the unmixing model represents a source type, not necessarily a single physical source. Multiple facilities in Port Angeles burning salt-laden wood wastes in an HFB are likely to have had similar dioxin TEQ profiles. Therefore, the soil TEQ mass calculated from sampling results in this study could reflect contributions from more than one HFB source. The Daishowa, K-Ply, and Fibreboard facilities are located 1.5 to 3 miles west of the former Rayonier mill, generally upwind of the areas sampled in this study according to available wind roses. Published studies have shown that impacts to nearby soils from air emissions sources of dioxins decrease relatively rapidly as distances from the source increase. The largest impacts from these other upwind HFBs in the study area for this report are therefore expected to occur within the western portion of the study area; interestingly, there are several relatively elevated Source 3

TEQ increments in soils within the westernmost sampling zone W3 (see Figure 8-20). Rapidly decreasing, but non-zero, contributions from these upwind HFBs may extend farther eastward throughout the study area. The eastern sampling zones are at distances great enough from the other HFBs that the impacts from their emissions to soils are expected to be slight. The Source 3–related mass of dioxins in soils was recalculated including only sampling zones E1, E2, and E4. The result was 4.5 grams TEQ, compared with 7.5 grams TEQ for the entire study area. Considering long-range transport of most of the emitted dioxins (Lohman and Seigneur 2001), the soil Source 3 TEQ mass restricted to only eastern sampling zones would still indicate source emissions of tens of grams TEQ for a source located within the study area as opposed to upwind of the study area.

Residential wood burning in Port Angeles. The TEQ profiles for residential wood burning (see examples in Appendix D) are most similar to Source 3 among the three unmixing analysis source profiles, although they are somewhat less similar (by correlations or principal components plots) to Source 3 than the salt-laden wood burning HFB TEQ profiles are. Residential wood burning activities can be assumed to be widely distributed throughout Port Angeles rather than localized to specific blocks. To the extent that it contributes to the Source 3 TEQ increments in soils, residential wood burning may therefore have relatively homogenous spatial impacts. Studies of soil dioxins/furans in other communities where wood burning is likely to be relatively common (e.g., Denver, Colorado and Trondheim, Norway) indicate that its impact on soil TEQs is likely to be no more than a few ng TEQ/kg on average.

Data on the annual amounts of (salt-laden) wood burned in the Rayonier HFB are available from an Ecology Annual Emission Inventory (Wilson 2011). Between 1979 and 1991, those annual amounts ranged between 93,500 and 180,000 tons and averaged more than 133,000 tons per year. Estimates of the total amount of residential wood burning for all residences in Port Angeles were developed using information from several Pacific Northwest surveys of the use of fireplaces, inserts, and wood stoves (Otterson 2011) and specific census data (2005–2009 American Community Survey) for residences in Port Angeles and Clallam County (U.S. Census Bureau 2011). A range of 10,000 to 20,000 tons per year, depending on assumptions, is considered representative for total residential wood burning in Port Angeles (at current population levels). On an annualized basis, therefore, the former Rayonier Mill HFB burned many times more wood than total residential use, and salt-laden wood as opposed to non-salt-laden wood. The Rayonier HFB, as a localized point source, would also be much more likely to have a spatial gradient for soil impacts rather than a homogeneous spatial impact.

Port Angeles medical waste incinerator. Given the source increment spatial pattern mapping for Source 3 (see Section 8.3.4 and Figure 8-20), potential sources located close to the Rayonier HFB stack are of greatest interest for additional cumulative emissions estimates. One potential dioxin emissions source located near the Rayonier HFB stack was the former medical waste incinerator at Olympic Medical Center. No stack test data are available for that facility. TEQ profiles developed from stack tests at other medical waste incinerators are distinctly different than TEQ profiles for HFBs burning salt-laden wood and are not similar to the Source 3 profile from the unmixing analysis; TEQ profiles from two other Washington medical waste incinerators (developed from data in Yake et al. 1998) are included in Appendix D. Even absent a facility-specific stack test for the former Port Angeles incinerator, the information on chemical TEQ profiles for this class of sources makes it highly unlikely that it is a significant source for the Source 3 TEQ increments in soil.

Yake et al. (1998) provide dioxin emissions estimates for two other Washington state medical waste incinerators, at the Veteran's Administrative Medical Center and Northwest Hospital, each based on the average of three sampling runs from 1995. Those estimates are 0.540 mg TEQ/day and 0.146 mg TEQ/day, compared with the Rayonier Mill HFB estimate of 0.168 mg TEQ/day (all values as reported by Yake et al. using earlier TEFs). The Olympic Medical Center incinerator was closed in 1990; available information indicates it operated for approximately 15 years. The scale of operations (e.g., number of hours of operation per year) at the Port Angeles incinerator is believed to have been less than that at either of the other two incinerators characterized by Yake et al. (1998). The emissions values cited above are therefore likely to be upper bounds for the Port Angeles incinerator. Applying those estimates to a 15-year operating period produces cumulative emissions estimates of 0.8 to 3 grams TEQ, which would be only marginally higher if adjusted for current TEFs and treatment of ND congener results. The Port Angeles medical waste incinerator, therefore, does not appear to be a credible source of cumulative emissions on the order of tens of grams TEQ.

Mass balance evaluation summary. The approach and conclusions for the mass balance evaluations, based on Source 3 increments with a TEQ profile similar to emissions from HFBs burning salt-laden wood, are summarized as follows:

- Given the limited data available and the number of assumptions required to complete a Source 3 TEQ increments mass balance, the evaluations provided here are considered exploratory.
- Based on the results of unmixing chemometric analyses, Source 3 increments were estimated for each sample.
- The total mass of Source 3–related TEQ in sampled soils (0- to 3-inch depth interval over the entire study area) was calculated using a stratified (sampling zones) calculation approach. Using 70 of the 85 samples in this study, the calculated mass is approximately 7.5 grams TEQ.
- Accounting for the fact that only a small fraction of air-emitted dioxins are deposited locally (Lohman and Seigneur 2001), the calculated Source 3 TEQ mass in soils indicates cumulative source emissions (from one or multiple physical sources) on the order of tens of grams TEQ.
- Using current toxicity equivalency factors (TEFs), the only available Rayonier HFB stack test (in 1995) results in an estimated annual TEQ mass emissions rate of 0.077 grams TEQ/year.
- Dioxin emissions were almost certainly higher in the early decades of the 67 years of operations at the Rayonier Mill, although no measurements of early emissions are available. The 16-fold reduction in HFB particulate emissions that was reported after upgrading of pollution control systems supports a conclusion that dioxin emissions over much of Rayonier's operating history were higher than those measured in 1995.

- Rayonier's HFB stack appears to be a credible source for cumulative dioxin emissions on the order of tens of grams TEQ.
- A 2009 stack test at the Nippon mill, when non-salt-laden wood was being burned in the HFB, resulted in estimated annual emissions of 0.0033 grams TEQ/year. Compared to the annual emissions estimate from the 1995 Rayonier HFB stack test, where salt-laden wood was being burned, this supports the conclusion cited in the literature that burning salt-laden wood can substantially increase dioxin emissions.
- Other large wood-products industry facilities that have operated in Port Angeles are likely to have also burned salt-laden wood wastes in HFBs, although no data are available to characterize dioxin emissions resulting from such practices at those facilities. The dioxin TEQ profiles from multiple facilities burning salt-laden wood wastes in HFBs are likely to be similar. Based solely on narrative operating histories and the scale of these other plants, their combined (and in some cases individual) cumulative over time dioxin emissions may well have totaled tens of grams TEQ, similar to the estimates for the former Rayonier Mill HFB.
- Other facilities with potentially significant cumulative HFB dioxin emissions are located several miles west of the former Rayonier Mill, generally upwind of areas sampled in this study. The largest impacts from those HFB emissions in the study area for this report are expected within the western portion of the study area; several locations with elevated Source 3 TEQ increments occur within the westernmost sampling zone W3. Rapidly decreasing, but non-zero, contributions from the upwind HFBs may extend farther eastward throughout the study area.
- The calculated soil mass for Source 3 increments restricted to only the east sampling zones (E1, E2, and E4) is 4.5 grams TEQ, which still indicates cumulative source emissions on the order of tens of grams. The distance from the upwind HFBs to the eastern sampling zones is considered sufficient to limit their contributions to small increments. This restricted soil mass calculation therefore suggests one or more sources with Source 3 TEQ profiles and emissions on the order of tens of grams located within rather than upwind of the study area.
- Residential wood burning may have a TEQ profile similar to Source 3 from the unmixing analysis. Contributions to mapped Source 3 increments from residential wood burning are expected to be spatially homogeneous and limited in magnitude. The estimated total amount of wood burned by residents annually, the fact that it is largely non-salt-laden wood, and the data from other urban soil dioxin studies all support a conclusion of relatively small magnitude impacts from residential wood burning.
- A former medical waste incinerator operated for approximately 15 years at the Olympic Medical Center, located close to the former Rayonier Mill. No stack test data are available for that facility. Based on stack test results for dioxins at two other Washington State medical waste incinerators, the Olympic Medical Center incinerator is not a credible source for cumulative dioxin emissions of tens of grams TEQ. Even absent a facility-specific stack test for the former Port Angeles incinerator, information on TEQ profiles for this class of sources makes it highly unlikely that it is a significant source for the Source 3 increments in soil.

- The mass balance analysis considers possible contributions from several sources. Sources that could have contributed to the Source 3 TEQs in surface samples throughout the study area include the former Rayonier Mill HFB, several other HFBs located west (upwind) of the study area, and possibly residential wood burning throughout Port Angeles. Air emissions from residential wood burning are estimated to have had at most relatively small magnitude, spatially homogeneous contributions. Upwind HFBs that burned salt-laden wood, or that continue to burn non-salt-laden wood, are expected to have their greatest contributions to the study area for this report within the western portion of the study area, with decreasing contributions extending eastward throughout the study area. The former Rayonier Mill HFB is the primary Source 3-type source located within the study area and is centrally located with respect to many of the higher Source 3 increment soil concentrations. The upwind HFBs and the former Rayonier Mill HFB may have had comparable cumulative TEQ emissions, each at the appropriate order of magnitude to account for the mass of Source 3 increments measured in study area soils. Accurate quantitative estimates of source emissions are not possible because adequate facility-specific monitoring data are lacking.

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9.0 Summary

In this study, 85 surface soil samples (0 to 3 inches) were collected in and near Port Angeles, Washington, to characterize dioxin/furan concentrations and patterns in off-property areas around the former Rayonier Mill. Almost half of those samples (40 of 85) were found to have total TEQ concentrations greater than the MTCA Method B value of 11.1 ng TEQ/kg.

A primary objective of the study was to evaluate sources and their relative contributions to measured soil TEQ concentrations. Data evaluations addressed four lines of evidence:

- Magnitude
- Spatial Pattern
- Chemical Pattern
- Mass Balance

Multivariate chemometric analyses (unmixing analyses) of the soil dioxin/furan dataset played an important role in source evaluations. Once unmixing analyses of the TEQ profiles of soil samples partitioned total TEQ into separate source-related increments, the initial evaluations of magnitude and spatial pattern based on total TEQ results were refined by considering source increments. Those source increment results were also used in an initial mass balance evaluation.

The evaluations for each line of evidence are summarized as follows:

TEQ magnitude summary. The approach and conclusions for the evaluation of the total TEQ results for Port Angeles soil samples are summarized as follows:

- Total TEQ results were variable, ranging from 0.80 to 76.3 ng TEQ/kg.
- A small number of high outlier TEQ concentrations occurred, consistent with observations in other soil dioxin studies.
- TEQ concentrations in the most rural portion of the soil dioxins/furans study area—the upslope transects—were far lower than in the developed urban areas of Port Angeles.
- Almost half (40 of 85) of the samples had TEQ values exceeding Ecology’s Method B value of 11.1 ng TEQ/kg, including 33 of 60 grid-type samples.
- TEQ comparisons across sample types are affected by differences in the sampled areas for each type. Upslope transect and roadside-type samples in this study had lower median TEQ concentrations than grid and forest sample types.
- Although median TEQs were similar for grid- and forest-type sample subgroups, forest-type samples included a number of the higher TEQ results. Elevated TEQs in forest soils (a consequence of land cover) are consistent with the site conceptual model, especially given the locations of most forest-type samples well outside the Port Angeles urban core.
- Compared with available soil dioxin results from other locations, which are reasonably consistent with one another, soil dioxin TEQs in Port Angeles appear to be shifted higher.

This suggests that one or more local sources may have contributed to moderately elevated soil TEQs.

- TEQs for the upslope transect-type samples, well outside the developed Port Angeles area, are similar to Washington statewide and U.S. rural sampling results.

Total TEQ spatial pattern summary. The approach and conclusions for the evaluation of spatial patterns of soil dioxins based on total TEQ concentrations are summarized as follows:

- Distance and distance/direction versus TEQ scatter plots (one-dimensional) and a dot map (two-dimensional) were used to evaluate spatial patterns for total TEQ results.
- The expected difference in total TEQ concentrations between urban and rural areas was confirmed, with markedly lower values for the upslope transect locations compared with urbanized areas of Port Angeles, and generally lower values in the less-developed easternmost sampling areas.
- Apart from the urban-to-rural gradient, no simple gradients or trends were evident for total TEQs within the urban portion of the study area, even if the evaluation was limited to only grid-type samples (n=60) to reduce potential confounding from multiple sample types.
- Instances of high local variability in total TEQs for closely spaced sampling locations occurred, consistent with the conceptual model of comparatively high variability in developed areas where soil-disturbing activities and property-specific dioxin sources are likely.
- A few high-outlier total TEQ results appear anomalous compared with other nearby sampling locations.
- Grid-type sampling locations that exceed the MTCA Method B value of 11.1 ng TEQ/kg are widespread in developed areas of Port Angeles.
- The absence of clear spatial patterns in total TEQs that can be related to any single dioxin emissions source is influenced by the contributions from multiple dioxin sources across Port Angeles, as well as by varying individual property histories (soil-disturbing activities that dilute or reduce accumulated soil dioxin levels, and property-specific dioxin sources).

Unmixing analysis summary. The approach and conclusions for the multivariate evaluations of chemical patterns in the Port Angeles soil samples (unmixing analyses) are summarized as follows:

- Normalized TEQ profiles for the soil samples were developed as the basis for unmixing analyses, which used multivariate PCA and ALS techniques.
- PCA analyses and additional outlier detection methods identified 2 samples with unusual TEQ profiles; unmixing analyses were based on the remaining 83 samples.
- Three sources were determined sufficient to account for almost all (99.7%) of the variance in TEQ profiles across samples.

- The final unmixing model provided distinct TEQ profiles for each of 3 sources.
- The fractional contributions of each source profile to each soil sample were determined by the unmixing analyses, for all 85 samples (including 2 outliers); these results provide a partitioning, or decomposition, of total TEQs for samples into portions contributed by separate source profiles.
- Comparing the unmixing model TEQ profiles to measured TEQ profiles, the differences (residuals, for each congener contributing to TEQ) are small, demonstrating a high degree of goodness-of-fit for the model results.
- Interpretations of the 3 source profiles from unmixing analyses included compilation and review of a large number of characteristic source profiles, among which were numerous stack test results from HFBs burning salt-laden wood.
- Source 1, dominated by a single congener (2,3,7,8-TCDD), is similar to a tire burning profile and the TEQ profile for incidental dioxin formation during 2,4,5-T production.
- Source 2 is similar to a composite urban dioxins TEQ profile, including vehicle emissions; it is also similar to some HFB profiles, and may reflect a composite profile to some degree due to widespread co-occurrence of both typical urban and HFB sources in Port Angeles.
- Source 3 has strong similarity to the TEQ profile for stack emissions from a HFB burning salt-laden wood.

Source increment magnitude summary. The approach and conclusions for the evaluation of source increments for Port Angeles soil samples are summarized as follows:

- The unmixing model results were used to calculate TEQ increments from each of three source profiles for each of the 85 soil samples.
- Source 3 has a large contribution to total TEQ for many of the sampled locations; for grid-type samples, subtracting the Source 3 increments reduces the median TEQ by almost 60%.
- After subtracting Source 3 increments for grid-type samples, the remaining sample TEQs (sum of contributions from Sources 1 and 2) are similar to total TEQ results from other studies of urban soils; including Source 3 increments, the distribution of grid-type samples appears shifted higher compared to other studies of urban soils.
- After subtracting Source 3 increments for grid-type samples, remaining TEQs greater than 10 ng TEQ/kg are dominated by Source 1 contributions (10 of 11 cases); all Source 2 increments for grid-type samples are less than 9.7 ng TEQ/kg, with 47 out of 60 (78%) less than 5 ng TEQ/kg.
- Source 3 dominates most forest-type samples (greater than 70% contribution for 11 of 14 samples). After subtracting Source 3 increments, 12 of 14 forest-type samples have remaining TEQs less than 4 ng TEQ/kg, comparable to or lower than the TEQs for forest-type samples in the Washington statewide survey (Rogowski et al. 1999). The two higher remaining TEQs (8.96 and 23.6 ng TEQ/kg) are dominated by Source 2 contributions and are located near a major roadway and a landfill with heavy equipment operations.

- Source 3 has only minor contributions to two roadside-type samples collected outside of heavily developed areas of Port Angeles.
- Source 3 has large contributions to many of the upslope transect-type samples (57% to 81% for 6 of 9 samples), although Source 3 increments and total TEQs are low. This result was not anticipated as part of the Conceptual Site Model.
- Source 3 has the largest influence on the number of sample locations exceeding 11 ng TEQ/kg. Of the 40 samples out of 85 total locations that have total TEQs above 11 ng TEQ/kg, the number remaining if individual source increments are omitted is 25 without Source 1, 27 without Source 2, and only 12 without Source 3.
- Among the 15 samples with the highest total TEQ results (greater than 20 ng TEQ/kg), Source 1 alone contributes approximately 50% or more of total TEQ and more than 11 ng TEQ/kg to nine locations. Source 1 thus has the major influence on a subset of the samples with highest total TEQ results.

Source increment spatial pattern summary. The approach and conclusions for the evaluation of spatial patterns for the source increments determined by unmixing analyses are summarized as follows:

- Two-dimensional spatial mapping of soil total TEQ results was refined using source increment results from unmixing analyses.
- Concentration maps (“dot maps”) for all samples coded by sample type were prepared for each of three separate source increment datasets, to evaluate patterns related to specific source profiles. A contour plot (using the Nearest Neighbor contouring technique) was also developed for Source 3 TEQ increments to further illustrate spatial patterns for those source increments.
- Source 1 increments show widely distributed, isolated “hot spots,” consistent with property-specific dioxin/furan sources (e.g., tire burning or, possibly, chemical application of the herbicide 2,4,5-T), with most values (43 of 60 grid locations, or 72%) less than 3 ng TEQ/kg. Source 1 increments at all forest, road, and upslope sampling locations are small.
- Source 2 increments show a relatively even spatial distribution with many low concentrations (47 of 60 grid locations, or 78%, less than 5 ng TEQ/kg) and a small number of higher outlier values up to 9.7 ng TEQ/kg. Of all road, forest, and upslope sampling locations, only two forest sampling locations have higher outlier values for Source 2 increments.
- In contrast to Sources 1 and 2, Source 3 increments show strong spatial patterning with clusters of high values close to the former Rayonier Mill HFB stack, with 26 of 60 (43%) grid locations greater than 5 ng TEQ/kg and 10 of 60 (17%) greater than 10 ng TEQ/kg. Road and upslope Source 3 increments are small; forest sampling locations have comparatively elevated Source 3 increments, with 6 of 14 locations above 10 ng TEQ/kg.

- One cluster southeast of the former Rayonier Mill HFB stack (in the Gale's Addition area) is proximate to and generally downwind of the HFB location.[21]
- A second cluster southwest of the former Rayonier Mill HFB stack is proximate to the HFB location, but not in a dominant downwind direction according to the wind roses from Ediz Hook. The representativeness of those off-site wind roses is uncertain. The spatial pattern and proximity of these elevated Source 3 increments to the southwest, as well as observations of Rayonier HFB stack plume behavior and the distance to other Port Angeles HFBs assumed to have similar Source 3 profiles, are factors to consider in evaluating any connection between this southwest cluster and the Rayonier HFB. A former medical waste incinerator co-located with the southwest cluster has no stack test data but the TEQ profile for this type of source is not similar to the Source 3 profile.
- Beyond the proximate areas of higher Source 3 increments, values at grid sampling locations fall off substantially to the east and the south.
- Several higher Source 3 increments occur at the far western end of the soil dioxins/furans study area, closer to other potential HFB sources in Port Angeles. With available wind rose data, these additional higher Source 3 increment locations would be largely downwind of the other potential HFB sources and upwind of the Rayonier Mill. As distances to the west from the former Rayonier mill increase, higher contributions from other HFBs are more likely.
- Source 3 increments contribute more than 40% to total TEQ concentrations for 38 of 41 (93%) grid- and forest-type samples in the eastern sampling zones, and 17 of 33 (52%) in western sampling zones. Source 3 has the highest TEQ increment of the three sources for 34 of 41 samples in the east zones, and for 16 of 33 western samples.
- The inverse distance relationship from the Rayonier HFB location for Source 3 increments, with a Source 3 TEQ profile similar to emissions from HFBs burning salt-laden wood, provides evidence that those HFB stack emissions have impacted off-property soils. Source 3 increments generally decrease, but not to zero, as distance from the Rayonier HFB increases (both upwind and downwind). In addition to the Rayonier HFB, other Port Angeles sources with a similar TEQ profile may contribute to Source 3 TEQ increments as mapped.
- Urban-to-rural gradients in total TEQs, Source 2 increments, and Source 3 increments, but not Source 1 increments, are shown in distance versus TEQ concentrations for east zone plus upslope samples.

Mass balance evaluation summary. The approach and conclusions for the mass balance evaluations, based on Source 3 increments with a TEQ profile similar to emissions from HFBs burning salt-laden wood, are summarized as follows:

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[21] The general terms upwind and downwind are used in this report to reflect the dominant annual wind directions as shown in available Port Angeles wind roses. These terms should not be misunderstood to be absolute or exclusionary: for example, locations denoted as upwind may nonetheless have been downwind for a comparatively small fraction of an annual period, as reflected in a wind rose, and therefore would not be constantly or universally upwind.

- Given the limited data available and the number of assumptions required to complete a Source 3 TEQ increments mass balance, the evaluations provided here are considered exploratory.

- Based on the results of unmixing chemometric analyses, Source 3 increments were estimated for each sample.
- The total mass of Source 3–related TEQ in sampled soils (0- to 3-inch depth interval over the entire study area) was calculated using a stratified (sampling zones) calculation approach. Using 70 of the 85 samples in this study, the calculated mass is approximately 7.5 grams TEQ.
- Accounting for the fact that only a small fraction of air-emitted dioxins are deposited locally (Lohman and Seigneur 2001), the calculated Source 3 TEQ mass in soils indicates cumulative source emissions (from one or multiple physical sources) on the order of tens of grams TEQ.
- Using current toxicity equivalency factors (TEFs), the only available Rayonier HFB stack test (in 1995) results in an estimated annual TEQ mass emissions rate of 0.077 grams TEQ/year.
- Dioxin emissions were almost certainly higher in the early decades of the 67 years of operations at the Rayonier Mill, although no measurements of early emissions are available. The 16-fold reduction in HFB particulate emissions that was reported after upgrading of pollution control systems supports a conclusion that dioxin emissions over much of Rayonier's operating history were higher than those measured in 1995.
- Rayonier's HFB stack appears to be a credible source for cumulative dioxin emissions on the order of tens of grams TEQ.
- A 2009 stack test at the Nippon mill, when non-salt-laden wood was being burned in the HFB, resulted in estimated annual emissions of 0.0033 grams TEQ/year. Compared to the annual emissions estimate from the 1995 Rayonier HFB stack test, where salt-laden wood was being burned, this supports the conclusion cited in the literature that burning salt-laden wood can substantially increase dioxin emissions.
- Other large wood-products industry facilities that have operated in Port Angeles are likely to have also burned salt-laden wood wastes in HFBs, although no data are available to characterize dioxin emissions resulting from such practices at those locations. The dioxin TEQ profiles from multiple locations burning salt-laden wood wastes in HFBs are likely to be similar. Based solely on narrative operating histories and the scale of these other plants, their combined (and in some cases individual) cumulative over time dioxin emissions may well have totaled tens of grams TEQ, similar to the estimates for the former Rayonier Mill HFB.
- Other facilities with potentially significant cumulative HFB dioxin emissions are located several miles west of the former Rayonier Mill, generally upwind of areas sampled in this study. The largest impacts from those HFB emissions in the study area for this report are expected within the western portion of the study area; several locations with elevated Source 3 TEQ increments occur within the westernmost sampling zone W3. Rapidly

decreasing, but non-zero, contributions from the upwind HFBs may extend farther eastward throughout the study area.

- The calculated soil mass for Source 3 increments restricted to only the east sampling zones (E1, E2, and E4) is 4.5 grams TEQ, which still indicates cumulative source emissions on the order of tens of grams. The distance from the upwind HFBs to the eastern sampling zones is considered sufficient to limit their contributions to small increments. This restricted soil mass calculation therefore suggests one or more sources with Source 3 TEQ profiles and emissions on the order of tens of grams located within rather than upwind of the study area.
- Residential wood burning may have a TEQ profile similar to Source 3 from the unmixing analysis. Contributions to mapped Source 3 increments from residential wood burning are expected to be spatially homogeneous and limited in magnitude. The estimated total amount of wood burned by residents annually, the fact that it is largely non-salt-laden wood, and the data from other urban soil dioxin studies all support a conclusion of relatively small magnitude impacts from residential wood burning.
- A former medical waste incinerator operated for approximately 15 years at the Olympic Medical Center, located close to the former Rayonier Mill. No stack test data are available for that facility. Based on stack test results for dioxins at two other Washington State medical waste incinerators, the Olympic Medical Center incinerator is not a credible source for cumulative dioxin emissions of tens of grams TEQ. Even absent a facility-specific stack test for the former Port Angeles incinerator, information on TEQ profiles for this class of sources makes it highly unlikely that it is a significant source for the Source 3 increments in soil.
- The mass balance analysis considers possible contributions from several sources. Sources that could have contributed to the Source 3 TEQs in surface samples throughout the study area include the former Rayonier Mill HFB, several other HFBs located west (upwind) of the study area, and, possibly, residential wood burning throughout Port Angeles. Air emissions from residential wood burning are estimated to have had at most relatively small magnitude, spatially homogeneous contributions. Upwind HFBs that burned salt-laden wood, or that continue to burn non-salt-laden wood, are expected to have their greatest contributions to the study area for this report within the western portion of the study area, with decreasing contributions extending eastward throughout the study area. The former Rayonier Mill HFB is the primary Source 3–type source located within the study area and is centrally located with respect to many of the higher Source 3 increment soil concentrations. The upwind HFBs and the former Rayonier Mill HFB may have had comparable cumulative TEQ emissions, each at the appropriate order of magnitude to account for the mass of Source 3 increments measured in study area soils. Accurate quantitative estimates of source emissions are not possible because adequate facility-specific monitoring data are lacking.

Detailed evaluations of the soil dioxin/furan data collected in this study established several key findings. Total TEQ concentrations in Port Angeles soils are higher than in other available studies of urban soils. Unmixing analyses produced one source profile (Source 3) similar to emissions from HFBs burning salt-laden wood. The source increments from Source 3 account for the higher total TEQs in Port Angeles; subtracting them from total TEQs, the remaining TEQs are similar to those in other urban studies. The spatial pattern of source increments for grid-type samples from that modeled source shows a strong inverse distance relationship in relation to the Rayonier Mill HFB stack, with several outlying elevated source increments at the far western end of the study area. Exploratory mass balance analyses suggest that the former Rayonier Mill HFB and several other HFBs located west (upwind) of the study area may each have had cumulative TEQ emissions consistent with the required source emissions inferred from Source 3 increments mapping; the locations of these HFBs with respect to the study area influence their likely patterns of impacts.

Based on these evaluations, the major conclusion of this study is that dioxin/furan emissions from the former Rayonier Mill HFB stack have contributed to an elevation of TEQs in off-property soils in and near Port Angeles.

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Tables

Table 1-1 Dioxin/furan homologue groups and the 17 congeners of greatest concern

Homologue Group	Congener	Abbreviation
	Dioxins	
Tetrachlorodibenzo-*p*-dioxins		TCDD
	2,3,7,8-tetrachlorodibenzo-*p*-dioxin	2,3,7,8-TCDD
Pentachlorodibenzo-*p*-dioxins		PeCDD
	1,2,3,7,8-pentachlorodibenzo-*p*-dioxin	1,2,3,7,8-PeCDD
Hexachlorodibenzo-*p*-dioxins		HxCDD
	1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin	1,2,3,4,7,8-HxCDD
	1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin	1,2,3,6,7,8-HxCDD
	1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin	1,2,3,7,8,9-HxCDD
Heptachlorodibenzo-*p*-dioxins		HpCDD
	1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin	1,2,3,4,6,7,8-HpCDD
Octachlorodibenzo-*p*-dioxin	Octachlorodibenzo-*p*-dioxin	OCDD
	Furans	
Tetrachlorodibenzofurans		TCDF
	2,3,7,8-tetrachlorodibenzofuran	2,3,7,8-TCDF
Pentachlorodibenzofurans		PeCDF
	1,2,3,7,8-pentachlorodibenzofuran	1,2,3,7,8-PeCDF
	2,3,4,7,8-pentachlorodibenzofuran	2,3,4,7,8-PeCDF
Hexachlorodibenzofurans		HxCDF
	1,2,3,4,7,8-hexachlorodibenzofuran	1,2,3,4,7,8-HxCDF
	1,2,3,6,7,8-hexachlorodibenzofuran	1,2,3,6,7,8-HxCDF
	1,2,3,7,8,9-hexachlorodibenzofuran	1,2,3,7,8,9-HxCDF
	2,3,4,6,7,8-hexachlorodibenzofuran	2,3,4,6,7,8-HxCDF
Heptachlorodibenzofurans		HpCDF
	1,2,3,4,6,7,8-heptachlorodibenzofuran	1,2,3,4,6,7,8-HpCDF
	1,2,3,4,7,8,9-heptachlorodibenzofuran	1,2,3,4,7,8,9-HpCDF
Octachlorodibenzofuran	Octachlorodibenzofuran	OCDF

Table 3-1 Proposed sample distribution scheme

Sampling Zone/Target	Zone Area (square miles)	Number of Samples
W1	0.25	12
W2	0.93	16
W3	0.80	6
E1	0.32	24
E2	0.86	9
E3	0.25	6
E4	0.76	6
Targeted forested areas within Zones E2 and E4		10
North–south transects (Upslope)		9
Roadside locations		2
Total	*4.2*	*100*

Table 4-1 Distribution of collected samples by sample type

Sampling Zone/Target	Sample Type				
	Grid	Forest	Roadside	Transect	Subtotal
W1	10				10
W2	16	1			17
W3	6				6
E1	19				19
E2	5	6	1		12
E3	1				1
E4	3	7	1		11
Upslope				9	9
Total	*60*	*14*	*2*	*9*	*85*

Notes:

Samples designated as “grid” in the study design that were collected from forested properties are included here as “forest” samples.

Table 4-2 Summary of sample locations where charred wood was observed

Sampling Zone	Sample Location	charred wood observed at sampling property	sampling location moved to avoid charred wood	charred wood observed in collected sample
W1	W105	X	X	X
	W108	X	X	
	W109	X	X	
	W196	X	X	X
W2	W206	X	X	
	W299	X		X
W3	none			
E1	E105	X	X	
	E108	X	X	
	E109	X	X	
	E121	X		
	E194	X	X	
	E195	X	X	
E2	E298	X		
	E299	X	X	
E3	E302	X	X	
E4	E402	X	X	
	E403	X		
	E405	X		
	E499	X		X
Upslope transects	T103	X		
	T104	X	X	
Roadside	none			
Targeted forest	FF03	X	X	
	FF06	X		

Table 4-3 Summary of sample locations using modified subsample point configurations

Sampling Zone	Sample Locations
W1	W103, W105, W107, W108, W109, W196
W2	W202, W206, W209
W3	W303
E1	E105, E108, E109, E117, E194, E195, E196
E2	E204, E299
E3	E302
E4	E402
North-south transects (Upslope)	T104, T203, T301, T303
Targeted forest locations	FF03, FF05, FF07
Roadside locations	RD02

Note: See Table 4-2 for sample collection locations that were moved because charred wood was observed to be present at a property. This table includes those charred wood sampling locations as well as additional locations where soil collection configurations were modified for other reasons.

Table 4-4 Summary of collected samples by sample type, distance, and direction

Wind Rose Direction	Distance from Hog Fuel Boiler Stack (feet)							Sample Type Totals	Total Count
	<2500	2500-5000	5000-7500	7500-10000	10000-12500	12500-15000	>15000		
E					G: 2 F: 3	G: 1 F: 1	G: 2	G: 5 F: 4	9
ESE		G: 7	G: 5	G: 1 F: 1	F: 3 R: 1	F: 2 R: 1	F: 1	G: 13 F: 7 R: 2	22
SE	G: 2	G: 5	G: 1	F: 1		F: 1	T: 1	G: 8 F: 2 T: 1	11
SSE		G: 2		G: 1			T: 3	G: 3 T: 3	6
S	G: 3		G: 2				T: 3	G: 5 T: 3	8
SSW	G: 1	G: 3 F: 1			T: 1	T: 1		G: 4 F: 1 T: 2	7
SW	G: 2	G: 2	G: 2					G: 6	6
WSW	G: 1	G: 2	G: 3	G: 1				G: 7	7
W	G: 1	G: 4	G: 1	G: 2	G: 1			G: 9	9
Subtotals: type	*G: 10*	*G: 25* *F: 1*	*G: 14*	*G: 5* *F: 2*	*G: 3* *F: 6* *R: 1* *T: 1*	*G: 1* *F: 4* *R: 1* *T: 1*	*G: 2* *F: 1* *T: 7*		
Total Count:	*10*	*26*	*14*	*7*	*11*	*7*	*10*	*G: 60* *F: 14* *R: 2* *T: 9*	*85*

Notes:
Samples designated as “grid” in the study design that were collected from forested land cover are included here as “forest” samples.

Key to sample types:
G = grid
F = forest
R = road
T = upslope transect

Table 5-1. Dioxin/furan and total organic carbon results for investigative samples.

	E102SS	E103SS	E105SS	E106SS	E108SS	E109SS	E110SS	E111SS	E112SS	E116SS	E117SS	E121SS	E122SS	E194SS	E195SS	E196SS
Congeners (ng/kg)																
Dioxins																
2,3,7,8-TCDD	4.81	5.98	1.56	2.68	1.49	3.26	0.414	1.6	1.8	0.726	0.99	0.422	4.46	0.823	0.948	0.334
1,2,3,7,8-PECDD	5.44	4.71	5.91	6.51	5.1	10.6	1.52	5.21	7.02	2.69	4.64	1.26	2.67	2.62	3.59	1.04
1,2,3,4,7,8-HXCDD	5.25	5.37	7.83	6.84	5.52	12.5	1.52	6.13	9.05	2.97	5.46	1.43	3.07	2.69	4	1.11
1,2,3,6,7,8-HXCDD	8.29	9.59	12.1	12.9	12.2	19.9	3.89	9.6	13.7	4.62	9.29	2.55	5.59	4.32	7.55	1.83
1,2,3,7,8,9-HXCDD	9.37	9.78	13	13.5	11.4	20.9	3.31	11.1	15.3	4.94	10.1	2.48	5.58	4.67	8.35	2.13
1,2,3,4,6,7,8-HPCDD	51.3	93	76.9	104	128	117	37.9	56.8	120	26.2	55.2	25.1	42.6	19.9	107	16.6
OCDD	139	338	200	455	683	300	225	128	1280	63.5	151	128	214	50.1	766	130
Sum	223.46	466.43	317.3	601.43	846.71	484.16	273.554	218.44	1446.87	105.646	236.68	161.242	277.97	85.123	897.438	153.044
Furans																
2,3,7,8-TCDF	4.22	4.88	5.18	6.75	4.74	11.9	1.43	6.5	7.99	2.97	4.24	1.36	2.66	2.34	3.35	0.702
1,2,3,7,8-PECDF	2.73	2.83	3.64	4.09	3.01	7.42	0.91	3.49	4.76	1.74	2.89	0.862	1.76	1.43 U	1.89	0.538
2,3,4,7,8-PECDF	3.23	3.36	4.11	5.52	3.72	8.94	1.2	4.16	5.92	2.03	3.45	1.09	2.11	1.74	2.36	0.665
1,2,3,4,7,8-HXCDF	1.76	2.4	2.72	3.86	2.86	5.99	1.03	2.72 U	4.11	1.37	2.41	0.914	1.31	1.17	1.64	0.471 J
1,2,3,6,7,8-HXCDF	1.87	1.75	2.45	4.02	2.59	5	0.843	2.42	3.62	1.07	1.93	0.664	1.29	0.924	1.38	0.435 J
1,2,3,7,8,9-HXCDF	0.204 J	0.232 J	0.273 J	0.271 J	0.26 J	0.527	0.07 UJ	0.248 J	0.353 J	0.149 J	0.243 J	0.093 J	0.168 J	0.151 J	0.163 J	0.061 J
2,3,4,6,7,8-HXCDF	1.53	1.64	2.11	4.14	2.51	4.14	0.859	1.95	3.21	0.987	1.65	0.648	1.11	0.865	1.24	0.384 J
1,2,3,4,6,7,8-HPCDF	6.97	8.26	7.5	30.8	23.7	12.3	7.86	5.52	9.76	2.79	5.91	5.09	6.01	2.17	6.26	2.59
1,2,3,4,7,8,9-HPCDF	0.559	0.744	0.804	2.5	1.72	1.46 U	0.397 J	0.636	1.07	0.315 J	0.623	0.374 J	0.501	0.243 J	0.548	0.242 J
OCDF	11	15.6	9.17	99.7	58.1	13.8	11.9	7.06	13.4	3.16	8.13	10.1	12.8	2.51	9.03	9.12
Sum	34.07	41.696	37.957	161.651	103.21	71.477	26.499	34.704	54.193	16.581	31.476	21.195	29.719	13.543	27.861	15.208
Sum_All Congeners	257.53	508.13	355.26	763.08	949.92	555.64	300.05	253.14	1501.06	122.23	268.16	182.44	307.69	98.67	925.30	168.25
Homolog Groups (ng/kg)																
Dioxins																
TOTAL TETRA-DIOXINS	285	306	432	345	302	806	53.3	426	543	162	308	52	184	110	184	36.9
TOTAL PENTA-DIOXINS	293	284	446	302	307	729	54.2	354	451	150	326	48.7	158	98.2	195	39.1
TOTAL HEXA-DIOXINS	282	271	404	317	309	649	60.9	336	481	132	304	48	161	89.3	172	39.8
TOTAL HEPTA-DIOXINS	92.3	160	132	179	201	206	64.9	98.2	208	47.1	99.9	46.9	89.1	36.8	229	31.6
OCDD	139	338	200	455	683	300	225	128	1280	63.5	151	128	214	50.1	766	130
Sum	1091	1359	1614	1598	1802	2690	458	1342	2963	555	1189	324	806	384	1546	277
Furans																
TOTAL TETRA-FURANS	78.2	79.4	105	141	84.3	233	28.5	121	153	51.5	90.2	26.2	57.7	47.1	64.7	17.2
TOTAL PENTA-FURANS	38.5	42.7	53.1	132	56.6	115	17.5	49.6	96	25.4	46.7	14.2	29	19.8	31.7	10.1
TOTAL HEXA-FURANS	21.5	22.3	25.7	78.3	44.1	51	14.2	18.5	46.6	11.8	21.8	10.3	14.7	7.73	18	5.65
TOTAL HEPTA-FURANS	18.7	19.9	16.2	108	62.7	24	19.8	12	20.7	5.55	13.4	11.7	16.3	4.16	17	8.57
OCDF	11	15.6	9.17	99.7	58.1	13.8	11.9	7.06	13.4	3.16	8.13	10.1	12.8	2.51	9.03	9.12
Sum	168	180	209	559	306	437	92	208	330	97	180	73	131	81	140	51
Sum_All Homologs	1259	1539	1823	2157	2108	3127	550	1550	3293	652	1369	396	937	466	1686	328
Physical Parameters (%)																
Total Organic Carbon	3.1	4.08	3.58	7.73	4.27	5.82	4.28	3.53	4.31	2.99	3.66	3.42	3.47	3.72	2.85	6.09
Other Characteristics																
Sample Type	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid
Distance From HFB (ft)	2948	2630	4142	4222	4569	4393	5127	3932	4683	4859	5034	5573	6434	1857	1995	3412
Direction From HFB (degrees)	130	136	122	135	123	132	136	109	115	107	118	119	122	127	136	142

Notes:

HFB = former Rayonier Mill hog fuel boiler

Sample E112SS was incorrectly labeled as W112SS in the field; laboratory results are listed under sample W112SS.

Key:

J = Concentration is estimated.

U = Analyte was not detected.

The values reported by the analytical laboratory for all "U" coded (not-detected) dioxin/furan results reflect sample-specific Estimated Detection Limits developed in accordance with Method 8290 requirements.

Table 5-1. Dioxin/furan and total organic carbon results for investigative samples.

	E197SS	E198SS	E199SS	E201SS	E204SS	E206SS	E208SS	E298SS	E299SS	E302SS	E402SS	E403SS	E405SS	E406SS	E498SS	E499SS
Congeners (ng/kg)																
Dioxins																
2,3,7,8-TCDD	11.9	1.19	1.18	1.69	0.815	1.11	0.389 U	0.943	0.519	0.561	0.484	5.37	2.87	0.392	1.02	16.7
1,2,3,7,8-PECDD	7.1	4.62	2.46	6.31	1.71	3.78	1.69	2.88	2.34	1.64	1.58	12.9	2.11	2.14	2.89	1.21
1,2,3,4,7,8-HXCDD	8.54	5.91	2.4	7.63	1.69	3.98	2.04	3.21	3.57	1.59	1.71	11.9	2.36	1.53	3.11	1.4
1,2,3,6,7,8-HXCDD	13.3	9.43	4.45	11.4	3.69	6.29	3.14	6.65	11	2.99	3.22	36.1	4.72	4.29	6.2	2.84
1,2,3,7,8,9-HXCDD	15.7	12	5.23	12	3.05	7.11	3.58	6.25	7.26	3.17	3.35	31.6	4.8	3.46	5.95	2.69
1,2,3,4,6,7,8-HPCDD	75.2	64.6	35.8	68.8	43.8	37.1	17.1	57.6	145	17.5	17	331	27.7	14.1	40.1	36.7
OCDD	173	187	155	141	252	96.9	26.8	387	1000	50.8	54.2	2230	86.7	31.2	272	251
Sum	304.74	284.75	206.52	248.83	306.755	156.27	54.739	464.533	1169.689	78.251	81.544	2658.87	131.26	57.112	331.27	312.54
Furans																
2,3,7,8-TCDF	6.89	5.96	2.05	7.02	2.39	4.83	2.01	3.43	1.85	2.3	2.23	11.7	2.55	1.77	3.46	1.86
1,2,3,7,8-PECDF	3.53	4.95	1.32	4.2	1.33	2.56	1.17	2.03	1.25	1.12	1.26	6.94	1.44	1.26	2.27	0.96
2,3,4,7,8-PECDF	4.54	6.78	1.58	5.08	1.54	3.28	1.37	2.77	1.62	1.48	1.47	12	1.77	4.14	2.8	1.23
1,2,3,4,7,8-HXCDF	2.84	6.1	1.68	2.77	1.31 U	1.79	0.824	1.44	1.9	0.729	0.837	15.8	1.01	2.33	1.67	0.779
1,2,3,6,7,8-HXCDF	2.78	5.62	1.2	2.8	0.925	1.75	0.722	1.5	2.3	0.832	0.909	11.6	0.97	4.91	1.49	0.655
1,2,3,7,8,9-HXCDF	0.298 J	0.398 J	0.109 J	0.313 J	0.111 J	0.2 J	0.099 J	0.175 J	0.167 J	0.119 J	0.077 U?	0.621	0.115 J	0.085 J	0.18 J	0.074 J
2,3,4,6,7,8-HXCDF	2.21	7.44	1.19	2.33	0.817	1.54	0.725	1.32	1.64	0.7	0.772	12.1	0.88	5.91	1.35	0.614
1,2,3,4,6,7,8-HPCDF	8.26	29.6	19.6	7.88	13.5	6.52	1.55	5.43	17.5	2.38	2.41	112	3.36	5.53	3.95	4.63
1,2,3,4,7,8,9-HPCDF	0.763	2.36	0.632	0.844	1.92	0.677	0.198 J	0.551	1.1	0.242 J	0.271 J	5.88	0.336 UJ	0.528	0.46 J	0.381 J
OCDF	11.5	20.9	29.4	11	89.1	23.1	1.13	13	22.5	2.06	3.13	266	6.56	2.42	4.97	21.7
Sum	43.611	90.108	58.761	44.237	112.943	46.247	9.798	31.646	51.827	11.962	13.366	454.641	18.991	28.883	22.6	32.883
Sum_All Congeners	348.35	374.86	265.28	293.07	419.70	202.52	64.54	496.18	1221.52	90.21	94.91	3113.51	150.25	86.00	353.87	345.42
Homolog Groups (ng/kg)																
Dioxins																
TOTAL TETRA-DIOXINS	638	293	92.7	509	66.2	199	110	199	115	64.3	80.8	294	124	46.2	161	71
TOTAL PENTA-DIOXINS	560	310	82.5	431	61.4	186	101	152	107	64.9	67.2	299	118	56	147	55.4
TOTAL HEXA-DIOXINS	481	304	88.5	352	70.8	168	101	163	147	67.7	73.4	432	117	69.6	156	57.6
TOTAL HEPTA-DIOXINS	133	116	64.6	118	74	63.5	29.3	104	236	32.7	32.3	576	51.8	28.2	74.1	65
OCDD	173	187	155	141	252	96.9	26.8	387	1000	50.8	54.2	2230	86.7	31.2	272	251
Sum	1985	1210	483	1551	524	713	368	1005	1605	280	308	3831	498	231	810	500
Furans																
TOTAL TETRA-FURANS	124	127	41.1	133	41.7	79.3	34.6	77.6	37.8	37	41.4	313	44.3	113	74	28.4
TOTAL PENTA-FURANS	56.7	82.3	21.8	52.3	22.6	38.1	16.2	36.8	26.4	18.4	18.5	434	22.8	329	36.8	15.3
TOTAL HEXA-FURANS	27.8	64.9	20.8	26.1	16.9	18.1	7.09	17.8	42.3	9.14	8.55	274	10.5	171	15.9	9.62
TOTAL HEPTA-FURANS	19	47.8	35.1	16.6	59.4	20	2.88	14.6	46.3	5.06	4.72	279	7.32	12.9	8.9	14.1
OCDF	11.5	20.9	29.4	11	89.1	23.1	1.13	13	22.5	2.06	3.13	266	6.56	2.42	4.97	21.7
Sum	239	343	148	239	230	179	62	160	175	72	76	1566	91	628	141	89
Sum_All Homologs	2224	1553	632	1790	754	892	430	1165	1780	352	384	5397	589	860	951	589
Physical Parameters (%)																
Total Organic Carbon	4.72	3	3.94	5.26	2.71	4.83	5.29	9.48	3.21	3.3	2.58	5.04	6.78	2.54	4.05	3.1
Other Characteristics																
Sample Type	Grid	Grid	Grid	Grid	Grid	Forested	Grid	Grid	Grid	Grid	Forested	Forested	Grid	Grid	Forested	Grid
Distance From HFB (ft)	3315	4326	2928	6405	9462	11220	12009	11180	5952	7568	12860	12831	15049	15196	11917	14940
Direction From HFB (degrees)	113	108	148	115	107	99	96	100	106	153	129	120	99	93	117	95

Notes:
HFB = former Rayonier Mill hog fuel boiler
Sample E112SS was incorrectly labeled as W112SS in the field; labtoratory results are listed under sample W112SS.

Key:
J = Concentration is estimated.
U = Analyte was not detected.

The values reported by the analytical laboratory for all "U" coded (not-detected) dioxin/furan results reflect sample-specific Estimated Detection Limits developed in accordance with Method 8290 requirements.

Table 5-1. Dioxin/furan and total organic carbon results for investigative samples.

	FF01SS	FF02SS	FF03SS	FF04SS	FF05SS	FF06SS	FF07SS	FF08SS	FF09SS	RD01SS	RD02SS	T101SS	T103SS	T104SS	T201SS	T202SS
Congeners (ng/kg)																
Dioxins																
2,3,7,8-TCDD	3.43	1.2	1.18	2.61	0.485	3.54	2.03	0.86	4.56	0.564	1.64	0.187	0.249	0.197	0.634	0.156
1,2,3,7,8-PECDD	10.4	3.31	3.1	7.34	1.66	10.2	5.96	2.49	13.5	2	0.926	0.601	0.83	0.67	2.11	0.463 J
1,2,3,4,7,8-HXCDD	8.91	3.36	3.25	6.98	1.74	10.1	5.1	2.59	13.7	2.28	0.878	0.677	0.738	0.733	1.94	0.453 J
1,2,3,6,7,8-HXCDD	18.4	5.16	4.86	10.6	2.7	16.4	8.63	4.01	20	8.23	2.43	1.65	1.38	3.14	4.21	1.11
1,2,3,7,8,9-HXCDD	26.5	5.47	5.45	8.76	3.12	17.6	10	4.15	23.2	5.56	2.18	1.72	1.78	2.08	4.53	1.35
1,2,3,4,6,7,8-HPCDD	152	30.2	24.3	55.1	16.5	77.6	47.7	20.8	93.3	113	36.2	14.5	9.25	31.4	22.8	8.13
OCDD	603	58.3	39.5	109	43.2	152	108	37.8	124	693	313	74.4	30	171	68.8	31.3
Sum	822.64	107	81.64	200.39	69.405	287.44	187.42	72.7	292.26	824.634	357.254	93.735	44.227	209.22	105.024	42.962
Furans																
2,3,7,8-TCDF	12.1	6.68	4.26	13.7	2	15.6	11	4.31	22.7	0.543	0.564 U	0.719	1.33	0.593	3.6	0.395
1,2,3,7,8-PECDF	7.04	3.51	2.68	6.69	1.3	9.09	5.04	2.29	12.1	0.733	0.437 J	0.475	0.724	0.396 J	1.85	0.286 J
2,3,4,7,8-PECDF	9.32	4.65	3.19	8.19	1.44	10.4	6.35	2.79	15.2	0.897	0.64	0.631	0.999	0.594	2.39	0.444 J
1,2,3,4,7,8-HXCDF	5.67	2.2	1.78	3.5	0.915	4.75	3.05	1.43	6.86	1.93	0.624	0.691 U	0.567	0.654	1.13 U	0.335 J
1,2,3,6,7,8-HXCDF	5.33	2.01	1.69	3.71	0.759	5.53	2.7	1.2	7.13	1.16	0.524	0.482	0.458 J	0.543	1.22	0.293 J
1,2,3,7,8,9-HXCDF	0.465 J	0.214 J	0.23 UJ	0.438 J	0.098 UJ	0.63	0.288 J	0.162 J	0.844	0.221 J	0.076 J	0.042 J	0.045 J	0.05 J	0.105 J	0.027 J
2,3,4,6,7,8-HXCDF	5.33	2.15	1.39	3.64	0.714	4.42	2.53	1.15	6.43	1.17	0.541	0.519	0.47 J	0.599	1.23	0.316 J
1,2,3,4,6,7,8-HPCDF	29.2	3.61	3.08	7.13	2.19	10.9	6.67	2.8	10.9	17.5	5.58	3.66	1.16	11.7	3.26	1.34
1,2,3,4,7,8,9-HPCDF	1.69	0.468 J	0.437 J	0.891	0.275 UJ	1.3	0.695	0.332 J	1.64	1.04	0.392 J	0.286 J	0.157 J	0.629	0.353 J	0.118 J
OCDF	39.1	3.45	2.38	11.2	3.15	12.1	6.05	2.43	7.23	30	11.9	10.2	1.13	26.8	3.37	2.64
Sum	115.245	28.942	21.117	59.089	12.841	74.72	44.373	18.894	91.034	55.194	21.278	17.705	7.04	42.558	18.508	6.194
Sum_All Congeners	937.89	135.94	102.76	259.48	82.25	362.16	231.79	91.59	383.29	879.83	378.53	111.44	51.27	251.78	123.53	49.16
Homolog Groups (ng/kg)																
Dioxins																
TOTAL TETRA-DIOXINS	286	161	161	383	64.1	530	247	132	739	22.7	28.1	16.4	25.1	21.2	63.6	14.4
TOTAL PENTA-DIOXINS	268	155	149	319	70.8	452	217	116	578	29.8	26.6	17.3	25.5	20.1	64.1	12.3
TOTAL HEXA-DIOXINS	325	128	135	208	71.2	410	206	97.3	566	59.4	30	24.7	27.9	31.5	73.3	16.6
TOTAL HEPTA-DIOXINS	257	51.3	42.6	93.7	29.4	139	86.5	36.9	165	213	67.2	27	16.7	52	41.6	15.5
OCDD	603	58.3	39.5	109	43.2	152	108	37.8	124	693	313	74.4	30	171	68.8	31.3
Sum	1739	554	527	1113	279	1683	865	420	2172	1018	465	160	125	296	311	90
Furans																
TOTAL TETRA-FURANS	217	105	83.7	217	31.4	310	168	77	411	11.5	13.8	12.3	27.8	13.5	64.9	10.5
TOTAL PENTA-FURANS	139	62.4	41.3	101	15.3	140	80.4	33.4	179	18.3	11.5	7.93	13.4	10	32.2	7.02
TOTAL HEXA-FURANS	85.5	23.1	15.3	34.9	7.04	51.8	27.1	13.4	64.7	39.8	10.4	4.94	5.29	13.8	12	4.55
TOTAL HEPTA-FURANS	59.8	6.92	5.68	13.9	4.22	21.2	12.5	5.48	19.9	49.2	14.3	7.9	2.06	33.2	5.93	3.37
OCDF	39.1	3.45	2.38	11.2	3.15	12.1	6.05	2.43	7.23	30	11.9	10.2	1.13	26.8	3.37	2.64
Sum	540	201	148	378	61	535	294	132	682	149	62	43	50	97	118	28
Sum_All Homologs	2279	754	675	1491	340	2218	1159	552	2854	1167	527	203	175	393	430	118
Physical Parameters (%)																
Total Organic Carbon	6.52	4.9	3.78	5.84	1.11	7.23	4.39	2.95	9.44	3.15	1.89	2.71	2.74	3.66	9.75	3.61
Other Characteristics																
Sample Type	Forested	Forested	Forested	Forested	Forested	Forested	Forested	Forested	Forested	Roadside	Roadside	Upslope	Upslope	Upslope	Upslope	Upslope
Distance From HFB (ft)	14606	15191	12723	11910	11805	8419	8903	12024	10614	13862	10457	14040	17613	11595	15621	17731
Direction From HFB (degrees)	111	108	100	99	113	105	130	119	96	113	114	194	190	204	172	169

Notes:
HFB = former Rayonier Mill hog fuel boiler
Sample E112SS was incorrectly labeled as W112SS in the field; laboratory results are listed under sample W112SS.

Key:
J = Concentration is estimated.
U = Analyte was not detected.

The values reported by the analytical laboratory for all "U" coded (not-detected) dioxin/furan results reflect sample-specific Estimated Detection Limits developed in accordance with Method 8290 requirements.

Table 5-1. Dioxin/furan and total organic carbon results for investigative samples.

	T203SS	T301SS	T302SS	T303SS	W102SS	W103SS	W104SS	W105SS	W107SS	W108SS	W109SS	W196SS	W197SS	W198SS	W201SS	W202SS
Congeners (ng/kg)																
Dioxins																
2,3,7,8-TCDD	0.315	0.192	0.155 U	0.073 J	2.16	1.01	2.91	3.87	15	1.01	1.12	0.104	14.5	3.4	1.53	5.65
1,2,3,7,8-PECDD	0.926	0.632	0.439 UJ	0.384 J	3.73	2.98	5.68	6.58	5.12	3.16	3.56	0.438 J	3.72	8.69	4.06	2.79
1,2,3,4,7,8-HXCDD	0.815	0.526 J	0.403 J	0.518 J	3.91	3.17	6.19	6.95	5.59	3.31	3.88	0.544	2.81	9.24	3.95	3.03
1,2,3,6,7,8-HXCDD	1.92	1.14	0.93	1.56	7.28	5.99	10.4	11.2	9.95	6.26	9.32	1.26	6.89	15.8	7.62	6.15
1,2,3,7,8,9-HXCDD	2.15	1.23	0.956	1.28	7.47	6.42	12	12.1	10.3	6.58	7.9	1.14	5.95	16.6	8.31	6.17
1,2,3,4,6,7,8-HPCDD	10.7	7.19	6.37	15.2	61.1	45.1	62.7	66.5	90.1	48.5	89	11.5	71.2	102	64.2	70.7
OCDD	34.6	28.7	26	66.2	312	199	163	225	436	467	555	54	447	443	340	787
Sum	51.426	39.61	35.253	85.215	397.65	263.67	262.88	332.2	572.06	535.82	669.78	68.986	552.07	598.73	429.67	881.49
Furans																
2,3,7,8-TCDF	1.15 U	1.13	0.456	0.381	4.76	4.23	6.8	6.04	5.54	4.48	3.42	0.238 U	2.39	10.1	6.22	3.29
1,2,3,7,8-PECDF	0.698	0.581	0.222 J	0.246 J	2.53	2.52	3.73	3.44	2.98	2.16	1.9	0.18 J	1.52	5.56	3.33	1.75
2,3,4,7,8-PECDF	0.884	0.699	0.296 J	0.316 J	3.14	3.43	4.63	4.25	3.45	2.99	2.3	0.25 J	1.98	6.93	4.38	2.5
1,2,3,4,7,8-HXCDF	0.649	0.46 J	0.247 UJ	0.28 J	2.12	2.57	2.82	2.94	2.57	2.06	1.75	0.231 J	1.48	4.17	2.77	2.09
1,2,3,6,7,8-HXCDF	0.452 J	0.324 J	0.201 J	0.267 J	2.16	2.03	2.75	2.78	2.24	1.89	1.66	0.193 J	1.61	3.94	2.78	1.61
1,2,3,7,8,9-HXCDF	0.047 J	0.08 J	0.027 UJ	0.075 UJ	0.172 J	0.176 J	0.284 J	0.277 J	0.223 UJ	0.144 UJ	0.173 J	0.17 U	0.127 J	0.379 J	0.244 J	0.129 J
2,3,4,6,7,8-HXCDF	0.475 J	0.356 J	0.197 J	0.238 J	1.7	2.07	2.38	2.22	2.06	1.8	1.54	0.17 U	1.52	3.5	2.98	1.65
1,2,3,4,6,7,8-HPCDF	1.43	1.16	0.964	1.04	9.6	12.9	9.82	8.45	12.7	15.3	17.9	1.45 J	13.4	17.2	14.8	23.6
1,2,3,4,7,8,9-HPCDF	0.166 J	0.154 J	0.091 J	0.113 J	0.775	0.696	0.923	0.811	1.01	1.01	1.1	0.085 J	0.904	1.48	1.1	1.35
OCDF	1.47	1.38	1.32	0.87 J	16.6	18	11.6	13.9	26.3	125	67.7	1.95	31.8	37.7	26.2	236
Sum	7.421	6.324	4.021	3.826	43.557	48.622	45.737	45.108	59.073	156.834	99.443	4.917	56.731	90.959	64.804	273.969
Sum_All Congeners	58.85	45.93	39.27	89.04	441.21	312.29	308.62	377.31	631.13	692.65	769.22	73.90	608.80	689.69	494.47	1155.46
Homolog Groups (ng/kg)																
Dioxins																
TOTAL TETRA-DIOXINS	23	20.9	9.05	8.39	208	174	328	441	291	191	154	9.19	116	542	223	142
TOTAL PENTA-DIOXINS	23.2	18.6	9.83	10.1	178	147	303	410	235	166	147	10.6	114	459	185	131
TOTAL HEXA-DIOXINS	29.6	19.7	13.8	16.4	184	142	299	380	238	157	141	14.7	118	439	163	141
TOTAL HEPTA-DIOXINS	21.2	14.2	12	27.7	95.8	74.5	100	109	158	84.3	157	20.3	123	181	116	123
OCDD	34.6	28.7	26	66.2	312	199	163	225	436	467	555	54	447	443	340	787
Sum	132	102	71	129	978	737	1193	1565	1358	1065	1154	109	918	2064	1027	1324
Furans																
TOTAL TETRA-FURANS	26	19.1	7.57	5.57	93.3	89.5	120	108	95.9	87.3	60.1	5.03	51.3	184	125	59
TOTAL PENTA-FURANS	12.2	8.95	3.84	4.06	45.2	52.7	61.2	57.1	47.7	51	35.2	3.1	47.2	93.2	63.9	43.1
TOTAL HEXA-FURANS	5.21	3.98	1.74	3.79	25.7	30	32.5	31.1	28.7	31.7	27.8	3.12	31.6	47	36.2	31.3
TOTAL HEPTA-FURANS	2.77	2.37	2.02	2.37	23.9	25.2	20.2	19.7	30.6	36.5	53.6	3.4	38	40.7	33.6	58.8
OCDF	1.47	1.38	1.32	0.87 J	16.6	18	11.6	13.9	26.3	125	67.7	1.95	31.8	37.7	26.2	236
Sum	48	36	16	17	205	215	246	230	229	332	244	17	200	403	285	428
Sum_All Homologs	179	138	87	145	1183	952	1439	1795	1587	1397	1398	125	1118	2467	1312	1752
Physical Parameters (%)																
Total Organic Carbon	6.11	3.76	3.64	4.18	4.27	3.03	7.96	4.05	4.32	2.97	5.49	1.29	6.98	4.8	6.01	4.23
Other Characteristics																
Sample Type	Upslope	Upslope	Upslope	Upslope	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid
Distance From HFB (ft)	20290	17577	18397	20615	3444	2605	1888	1355	1297	2127	2225	2270	1055	2320	4435	5370
Direction From HFB (degrees)	171	143	148	157	272	268	233	228	206	184	173	268	188	254	259	250

Notes:
HFB = former Rayonier Mill hog fuel boiler
Sample E112SS was incorrectly labeled as W112SS in the field; laboratory results are listed under sample W112SS.

Key:
J = Concentration is estimated.
U = Analyte was not detected.

The values reported by the analytical laboratory for all "U" coded (not-detected) dioxin/furan results reflect sample-specific Estimated Detection Limits developed in accordance with Method 8290 requirements.

Table 5-1. Dioxin/furan and total organic carbon results for investigative samples.

	W203SS	W204SS	W205SS	W206SS	W207SS	W208SS	W209SS	W210SS	W211SS	W212SS	W213SS	W214SS	W215SS	W216SS	W299SS	W301SS
Congeners (ng/kg)																
Dioxins																
2,3,7,8-TCDD	16.8	2.42	2.46	2.62	7.42	0.961	72	16.3	0.254	2.42	22	19.8	1.74	7.1	1.87	1.54
1,2,3,7,8-PECDD	2.48	7.14	2.64	4.29	2.8	2.14	1.64	4.39	0.661	1.23	2.99	2.68	2.35	2.86	4.72	4.88
1,2,3,4,7,8-HXCDD	2.37	6.93	3.06	5.14	2.84	2.15	1.63	4.25	0.671	1.29	2.4	2.64	2.49	2.72	4.35	3.94
1,2,3,6,7,8-HXCDD	6.02	11.8	8.61	12.2	5.45	4.26	3.76	7.69	1.43	4.04	6.21	7.44	4.49	10.8	7.81	7.2
1,2,3,7,8,9-HXCDD	5.55	13	7.88	11.6	5.68	4.35	3.62	8.06	1.58	3.43	5.09	5.22	4.66	8.91	8.35	8.11
1,2,3,4,6,7,8-HPCDD	85.1	70.8	85.5	124	38.7	40.1	37	49.1	14.3	50.1	57.6	124	34.4	206	39	42.4
OCDD	623	190	350	527	151	206	212	171	74.1	315	398	813	149	1920	101	170
Sum	741.32	302.09	460.15	686.85	213.89	259.961	331.65	260.79	92.996	377.51	494.29	974.78	199.13	2158.39	167.1	238.07
Furans																
2,3,7,8-TCDF	2.56	8.67	3.19	4.19	3.45	2.39	1.77	4.5	0.549	1.26	3.81	2.34	2.87	4.76	7.01	6.08
1,2,3,7,8-PECDF	1.4	4.33	1.59	2.63	1.95	1.32	0.967	2.74	0.346 J	0.759	1.92	1.41	1.39	2.26	3.85	3.38
2,3,4,7,8-PECDF	1.96	5.96	2.11	3.46	2.44	1.7	1.61	3.45	0.442 J	0.967	2.47	1.74	1.87	3.36	4.76	4.48
1,2,3,4,7,8-HXCDF	1.57	3.63	2.27	2.86	1.54	1.16	1.55	2.23	0.368 UJ	0.93	1.53	2.52	1.25	3.77	2.26	2.64
1,2,3,6,7,8-HXCDF	1.24	3.3	2.06	2.86	1.49	1.2	1.45	2.09	0.321 J	0.744	1.4	2.01	1.12	1.78	2.26	2.37
1,2,3,7,8,9-HXCDF	0.111 J	0.318 J	0.188 J	0.183 J	0.159 J	0.098 J	0.115 J	0.199 J	0.033 J	0.072 UJ	0.112 J	0.129 J	0.136 UJ	0.15 J	0.249 J	0.231 J
2,3,4,6,7,8-HXCDF	1.29	3.09	2.12	2.71	1.34	0.974	1.69	1.96	0.313 J	0.724	1.31	1.69	0.885	1.74	1.95	2.29
1,2,3,4,6,7,8-HPCDF	13.9	12	49.7	20.5	6.96	8.05	10.5	10.6	2.47	11.2	9.75	59.2	4.58	27.8	5.09	8.87
1,2,3,4,7,8,9-HPCDF	0.843	0.994	1.41	1.05	0.577	0.606	0.683	0.654	0.191 J	0.494	0.627	2.82	0.448 J	1.87	0.511	0.812
OCDF	62.6	17.6	45.7	36.1	10.8	22.8	18.8	13.5	4.2	16.1	20.8	169	8.25	73.4	5.76	12.5
Sum	87.474	59.892	110.338	76.543	30.706	40.298	39.135	41.923	9.233	33.25	43.729	242.859	22.799	120.89	33.7	43.653
Sum_All Congeners	828.79	361.98	570.49	763.39	244.60	300.26	370.79	302.71	102.23	410.76	538.02	1217.64	221.93	2279.28	200.80	281.72
Homolog Groups (ng/kg)																
Dioxins																
TOTAL TETRA-DIOXINS	96.9	423	139	257	147	128	125	256	16.8	60.6	114	114	127	72.2	217	197
TOTAL PENTA-DIOXINS	87.3	350	129	233	132	95.5	51.4	217	16.7	58.8	99.2	93.4	117	69.3	190	169
TOTAL HEXA-DIOXINS	102	343	153	253	136	104	67.2	205	23.3	79.7	100	109	103	119	198	156
TOTAL HEPTA-DIOXINS	156	123	154	203	72	62.9	67.3	87.8	27.8	88.7	102	203	61.2	360	74.6	72.6
OCDD	623	190	350	527	151	206	212	171	74.1	315	398	813	149	1920	101	170
Sum	1065	1429	925	1473	638	596	523	937	159	603	813	1332	557	2541	781	765
Furans																
TOTAL TETRA-FURANS	41.1	162	54.3	84.5	63.9	43.7	32.3	82.6	10.2	21.3	58.3	38.3	52.1	58.9	141	115
TOTAL PENTA-FURANS	30.1	77.7	31.9	57.7	33.7	26.4	37.4	46.7	5.8	14.3	36.8	25.5	25.2	36	65.6	51.9
TOTAL HEXA-FURANS	20.8	40.6	70.3	42.7	20.6	16.1	30.1	27	3.95	14.5	24.2	54.6	12.2	39.9	23.2	26.8
TOTAL HEPTA-FURANS	40.2	25.4	139	41.8	16.6	22	23	21.5	6.03	25.5	25.6	172	10.2	78.3	11.7	18.2
OCDF	62.6	17.6	45.7	36.1	10.8	22.8	18.8	13.5	4.2	16.1	20.8	169	8.25	73.4	5.76	12.5
Sum	195	323	341	263	146	131	142	191	30	92	166	459	108	287	247	224
Sum_All Homologs	1260	1752	1266	1736	784	727	665	1128	189	695	979	1792	665	2827	1028	989
Physical Parameters (%)																
Total Organic Carbon	3.57	4.34	4.53	3.68	7.13	3.13	4.21	5.08	6.77	4.15	2.04	4.51	3.12	7.53	2.9	5.24
Other Characteristics																
Sample Type	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Grid	Forested	Grid
Distance From HFB (ft)	7462	3583	4849	6328	3321	4408	6138	3302	4071	5294	3409	5349	4116	5489	4769	8973
Direction From HFB (degrees)	244	250	239	238	224	221	224	205	210	215	192	171	169	175	209	279

Notes:
HFB = former Rayonier Mill hog fuel boiler
Sample E112SS was incorrectly labeled as W112SS in the field; laboratory results are listed under sample W112SS.

Key:
J = Concentration is estimated.
U = Analyte was not detected.

The values reported by the analytical laboratory for all "U" coded (not-detected) dioxin/furan results reflect sample-specific Estimated Detection Limits developed in accordance with Method 8290 requirements.

Table 5-1. Dioxin/furan and total organic carbon results for investigative samples.

	W302SS	W303SS	W304SS	W305SS	W306SS
Congeners (ng/kg)					
Dioxins					
2,3,7,8-TCDD	2.38	1.78	13	0.98	4.69
1,2,3,7,8-PECDD	4.2	4.36	4.09	1.42	2.89
1,2,3,4,7,8-HXCDD	4.28	3.92	4.29	1.35	3.15
1,2,3,6,7,8-HXCDD	7.63	7.45	10.4	2.95	5.82
1,2,3,7,8,9-HXCDD	10	8.08	8.96	2.75	6.29
1,2,3,4,6,7,8-HPCDD	56.6	48.3	153	41.8	54.8
OCDD	271	169	1060	327	340
Sum	356.09	242.89	1253.74	378.25	417.64
Furans					
2,3,7,8-TCDF	9.48	5.58	4.35	1.62	4.01
1,2,3,7,8-PECDF	2.99	3.4	2.55	0.976	2.56
2,3,4,7,8-PECDF	5.68	3.82	3.38	1.31	3.19
1,2,3,4,7,8-HXCDF	3.75	2.16	2.7	0.965	2.17
1,2,3,6,7,8-HXCDF	2.41	2.25	2.07	0.724	2.12
1,2,3,7,8,9-HXCDF	0.182 J	0.223 J	0.205 J	0.069 J	0.194 J
2,3,4,6,7,8-HXCDF	2.25	2.12	2.14	0.813	2.2
1,2,3,4,6,7,8-HPCDF	12.7	9.77	16.8	9.44	12.8
1,2,3,4,7,8,9-HPCDF	0.987	0.867	1.26	0.649	1.01
OCDF	27.6	15.5	45.6	30	24.2
Sum	68.029	45.69	81.055	46.566	54.454
Sum_All Congeners	424.12	288.58	1334.80	424.82	472.09
Homolog Groups (ng/kg)					
Dioxins					
TOTAL TETRA-DIOXINS	190	214	191	59.5	160
TOTAL PENTA-DIOXINS	140	195	173	55.4	126
TOTAL HEXA-DIOXINS	146	184	199	56.2	135
TOTAL HEPTA-DIOXINS	102	85.2	248	67.9	97.3
OCDD	271	169	1060	327	340
Sum	849	847	1871	566	858
Furans					
TOTAL TETRA-FURANS	173	101	78.8	31.7	83.6
TOTAL PENTA-FURANS	93.1	52.1	46	17.2	50.2
TOTAL HEXA-FURANS	36.4	26.8	34.9	12	30.9
TOTAL HEPTA-FURANS	30.3	21.3	50	26.5	30.3
OCDF	27.6	15.5	45.6	30	24.2
Sum	360	217	255	117	219
Sum_All Homologs	1209	1064	2126	683	1078
Physical Parameters (%)					
Total Organic Carbon	5.62	3.01	5.23	1.92	4.01
Other Characteristics					
Sample Type	Grid	Grid	Grid	Grid	Grid
Distance From HFB (ft)	11497	7289	8525	4671	8776
Direction From HFB (degrees)	261	274	263	276	252

Notes:
HFB = former Rayonier Mill hog fuel boiler
Sample E112SS was incorrectly labeled as W112SS in the field; laboratory results are listed under sample W112SS.

Key:
J = Concentration is estimated.
U = Analyte was not detected.

The values reported by the analytical laboratory for all "U" coded (not-detected) dioxin/furan results reflect sample-specific Estimated Detection Limits developed in accordance with Method 8290 requirements.

Table 6-1 Summary statistics for TEQ results

Analyte/Sample Grouping	Number of Samples	Min. Detect Conc.	Max. Detect Conc.	Location of Max. Conc.	Mean Conc.	No. Samples >MTCA Method B	% Samples >MTCA Method B
Study-wide TEQ (ND = 0)	85	0.492	76.3	W209SS	12.7	40	47
Study-wide TEQ (ND = 0.5*DL)	85	0.800	76.3	W209SS	12.7	40	47
Study-wide TEQ, No Upslope (ND = 0.5*DL)	76	1.13	76.3	W209SS	14.0	40	53
All W Zones, Grid (ND = 0.5*DL)	32	1.13	76.3	W209SS	16.0	21	66
Zone W1 TEQ (ND = 0.5*DL)	10	1.11	26.3	W107SS	14.1	5	50
Zone W2 TEQ (ND = 0.5*DL)	16	1.76	76.3	W209SS	18.7	11	69
Zone W3 TEQ (ND = 0.5*DL)	6	4.57	23.7	W304SS	12.7	5	83
All E Zones, Grid (ND = 0.5*DL)	28	2.54	26.6	E197SS	11.2	12	43
Zone E1 TEQ (ND = 0.5*DL)	19	2.54	26.6	E197SS	12.4	10	53
Zone E2 TEQ (ND = 0.5*DL)	5	3.84	15.1	E201SS	8.03	1	20
Zone E3 TEQ (ND = 0.5*DL)	1	4.14	4.14	E302SS	--	0	0
Zone E4 TEQ (ND = 0.5*DL)	3	6.45	19.9	E499SS	11.3	1	33
Upslope TEQ (ND = 0.5*DL)	9	0.80	5.54	T201SS	2.14	0	0
Roadside TEQ (ND = 0.5*DL)	2	4.04	6.5	RD01SS	5.27	0	0
Forest TEQ (ND = 0.5*DL)	14	4.02	40.5	E403SS	15.8	7	50

Notes:

MTCA Method B is the soil TEQ concentration equivalent to a 1 in 1,000,000 cancer risk using the standard Method B equation for unrestricted land use (11.1 ng TEQ/kg).

All TEQ concentrations presented in ng/kg, dry weight.

Zone TEQs include grid-type samples only (do not include forest-type samples collected in respective zones or roadside-type samples).

Forest TEQs include all forest-type samples collected from all zones.

Upslope TEQs include samples from all three transects.

Study-wide TEQs includes all samples collected, including roadside, grid, upslope, and forest sample types.

Key:

MTCA = Model Toxics Control Act

ND = Non-detect.

TEQ = Total toxic equivalency quotient.

DL = Detection limit.

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Table 6-2. Normalized congeners and homolog results.

	E102SS	E103SS	E105SS	E106SS	E108SS	E109SS	E110SS	E111SS	E112SS	E116SS	E117SS	E121SS	E122SS	E194SS	E195SS	E196SS
Congeners (ng/kg)																
Dioxins																
2,3,7,8-TCDD	0.019	0.012	0.004	0.004	0.002	0.006	0.001	0.006	0.001	0.006	0.004	0.002	0.014	0.008	0.001	0.002
1,2,3,7,8-PECDD	0.021	0.009	0.017	0.009	0.005	0.019	0.005	0.021	0.005	0.022	0.017	0.007	0.009	0.027	0.004	0.006
1,2,3,4,7,8-HXCDD	0.020	0.011	0.022	0.009	0.006	0.022	0.005	0.024	0.006	0.024	0.020	0.008	0.010	0.027	0.004	0.007
1,2,3,6,7,8-HXCDD	0.032	0.019	0.034	0.017	0.013	0.036	0.013	0.038	0.009	0.038	0.035	0.014	0.018	0.044	0.008	0.011
1,2,3,7,8,9-HXCDD	0.036	0.019	0.037	0.018	0.012	0.038	0.011	0.044	0.010	0.040	0.038	0.014	0.018	0.047	0.009	0.013
1,2,3,4,6,7,8-HPCDD	0.199	0.183	0.216	0.136	0.135	0.211	0.126	0.224	0.080	0.214	0.206	0.138	0.138	0.202	0.116	0.099
OCDD	0.540	0.665	0.563	0.596	0.719	0.540	0.750	0.506	0.853	0.520	0.563	0.702	0.696	0.508	0.828	0.773
Sum	0.868	0.918	0.893	0.788	0.891	0.871	0.912	0.863	0.964	0.864	0.883	0.884	0.903	0.863	0.970	0.910
Furans																
2,3,7,8-TCDF	0.016	0.010	0.0146	0.0088	0.0050	0.0214	0.0048	0.0257	0.005	0.024	0.016	0.007	0.009	0.024	0.004	0.004
1,2,3,7,8-PECDF	0.011	0.006	0.0102	0.0054	0.0032	0.0134	0.0030	0.0138	0.003	0.014	0.011	0.005	0.006	0.014 U	0.002	0.003
2,3,4,7,8-PECDF	0.013	0.007	0.0116	0.0072	0.0039	0.0161	0.0040	0.0164	0.004	0.017	0.013	0.006	0.007	0.018	0.003	0.004
1,2,3,4,7,8-HXCDF	0.007	0.005	0.0077	0.0051	0.0030	0.0108	0.0034	0.0107 U	0.003	0.011	0.009	0.005	0.004	0.012	0.002	0.003 J
1,2,3,6,7,8-HXCDF	0.007	0.003	0.0069	0.0053	0.0027	0.0090	0.0028	0.0096	0.002	0.009	0.007	0.004	0.004	0.009	0.001	0.003 J
1,2,3,7,8,9-HXCDF	0.001 J	0.000 J	0.0008 J	0.0004 J	0.0003 J	0.0009	0.0002 UJ	0.0010 J	0.000 J	0.001 J	0.001 J	0.001 J	0.001 J	0.002 J	0.000 J	0.000 J
2,3,4,6,7,8-HXCDF	0.006	0.003	0.0059	0.0054	0.0026	0.0075	0.0029	0.0077	0.002	0.008	0.006	0.004	0.004	0.009	0.001	0.002 J
1,2,3,4,6,7,8-HPCDF	0.027	0.016	0.0211	0.0404	0.0249	0.0221	0.0262	0.0218	0.007	0.023	0.022	0.028	0.020	0.022	0.007	0.015
1,2,3,4,7,8,9-HPCDF	0.002	0.001	0.0023	0.0033	0.0018	0.0026 U	0.0013 J	0.0025	0.001	0.003 J	0.002	0.002 J	0.002	0.002 J	0.001	0.001 J
OCDF	0.043	0.031	0.0258	0.1307	0.0612	0.0248	0.0397	0.0279	0.009	0.026	0.030	0.055	0.042	0.025	0.010	0.054
Sum	0.132	0.082	0.1068	0.2118	0.1087	0.1286	0.0883	0.1371	0.036	0.136	0.117	0.116	0.097	0.137	0.030	0.090
Sum_All Congeners	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Homolog Groups (ng/kg)																
Dioxins																
TOTAL TETRA-DIOXINS	0.226	0.199	0.237	0.160	0.143	0.258	0.097	0.275	0.165	0.248	0.225	0.131	0.196	0.236	0.109	0.112
TOTAL PENTA-DIOXINS	0.233	0.185	0.245	0.140	0.146	0.233	0.099	0.228	0.137	0.230	0.238	0.123	0.169	0.211	0.116	0.119
TOTAL HEXA-DIOXINS	0.224	0.176	0.222	0.147	0.147	0.208	0.111	0.217	0.146	0.202	0.222	0.121	0.172	0.192	0.102	0.121
TOTAL HEPTA-DIOXINS	0.073	0.104	0.072	0.083	0.095	0.066	0.118	0.063	0.063	0.072	0.073	0.118	0.095	0.079	0.136	0.096
OCDD	0.110	0.220	0.110	0.211	0.324	0.096	0.409	0.083	0.389	0.097	0.110	0.323	0.228	0.108	0.454	0.396
Sum	0.867	0.883	0.885	0.741	0.855	0.860	0.833	0.866	0.900	0.851	0.868	0.817	0.861	0.825	0.917	0.846
Furans																
TOTAL TETRA-FURANS	0.062	0.052	0.058	0.065	0.040	0.075	0.052	0.078	0.046	0.079	0.066	0.066	0.062	0.101	0.038	0.052
TOTAL PENTA-FURANS	0.031	0.028	0.029	0.061	0.027	0.037	0.032	0.032	0.029	0.039	0.034	0.036	0.031	0.043	0.019	0.031
TOTAL HEXA-FURANS	0.017	0.014	0.014	0.036	0.021	0.016	0.026	0.012	0.014	0.018	0.016	0.026	0.016	0.017	0.011	0.017
TOTAL HEPTA-FURANS	0.015	0.013	0.009	0.050	0.030	0.008	0.036	0.008	0.006	0.009	0.010	0.030	0.017	0.009	0.010	0.026
OCDF	0.009	0.010	0.005	0.046	0.028	0.004	0.022	0.005	0.004	0.005	0.006	0.025	0.014	0.005	0.005	0.028
Sum	0.133	0.117	0.115	0.259	0.145	0.140	0.167	0.134	0.100	0.149	0.132	0.183	0.139	0.175	0.083	0.154
Sum_All Homologs	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Key:
J = Concentration is estimated.
U = Analyte was not detected.

Table 6-2. Normalized congeners and homolog results.

	E197SS	E198SS	E199SS	E201SS	E204SS	E206SS	E208SS	E298SS	E299SS	E302SS	E402SS	E403SS	E405SS	E406SS	E498SS	E499SS
Congeners (ng/kg)																
Dioxins																
2,3,7,8-TCDD	0.034	0.003	0.004	0.006	0.002	0.005	0.006 U	0.002	0.000	0.006	0.005	0.002	0.019	0.005	0.003	0.048
1,2,3,7,8-PECDD	0.020	0.012	0.009	0.022	0.004	0.019	0.026	0.006	0.002	0.018	0.017	0.004	0.014	0.025	0.008	0.004
1,2,3,4,7,8-HXCDD	0.025	0.016	0.009	0.026	0.004	0.020	0.032	0.006	0.003	0.018	0.018	0.004	0.016	0.018	0.009	0.004
1,2,3,6,7,8-HXCDD	0.038	0.025	0.017	0.039	0.009	0.031	0.049	0.013	0.009	0.033	0.034	0.012	0.031	0.050	0.018	0.008
1,2,3,7,8,9-HXCDD	0.045	0.032	0.020	0.041	0.007	0.035	0.055	0.013	0.006	0.035	0.035	0.010	0.032	0.040	0.017	0.008
1,2,3,4,6,7,8-HPCDD	0.216	0.172	0.135	0.235	0.104	0.183	0.265	0.116	0.119	0.194	0.179	0.106	0.184	0.164	0.113	0.106
OCDD	0.497	0.499	0.584	0.481	0.600	0.478	0.415	0.780	0.819	0.563	0.571	0.716	0.577	0.363	0.769	0.727
Sum	0.875	0.760	0.778	0.849	0.731	0.772	0.848	0.936	0.958	0.867	0.859	0.854	0.874	0.664	0.936	0.905
Furans																
2,3,7,8-TCDF	0.020	0.016	0.008	0.024	0.006	0.024	0.031	0.007	0.002	0.025	0.023	0.004	0.017	0.021	0.010	0.005
1,2,3,7,8-PECDF	0.010	0.013	0.005	0.014	0.003	0.013	0.018	0.004	0.001	0.012	0.013	0.002	0.010	0.015	0.006	0.003
2,3,4,7,8-PECDF	0.013	0.018	0.006	0.017	0.004	0.016	0.021	0.006	0.001	0.016	0.015	0.004	0.012	0.048	0.008	0.004
1,2,3,4,7,8-HXCDF	0.008	0.016	0.006	0.009	0.003 U	0.009	0.013	0.003	0.002	0.008	0.009	0.005	0.007	0.027	0.005	0.002
1,2,3,6,7,8-HXCDF	0.008	0.015	0.005	0.010	0.002	0.009	0.011	0.003	0.002	0.009	0.010	0.004	0.006	0.057	0.004	0.002
1,2,3,7,8,9-HXCDF	0.001 J	0.001 J	0.000 J	0.001 J	0.000 J	0.001 J	0.002 J	0.000 J	0.000 J	0.001 J	0.001 U?	0.000	0.001 J	0.001 J	0.001 J	0.000 J
2,3,4,6,7,8-HXCDF	0.006	0.020	0.004	0.008	0.002	0.008	0.011	0.003	0.001	0.008	0.008	0.004	0.006	0.069	0.004	0.002
1,2,3,4,6,7,8-HPCDF	0.024	0.079	0.074	0.027	0.032	0.032	0.024	0.011	0.014	0.026	0.025	0.036	0.022	0.064	0.011	0.013
1,2,3,4,7,8,9-HPCDF	0.002	0.006	0.002	0.003	0.005	0.003	0.003 J	0.001	0.001	0.003 J	0.003 J	0.002	0.002 UJ	0.006	0.001 J	0.001 J
OCDF	0.033	0.056	0.111	0.038	0.212	0.114	0.018	0.026	0.018	0.023	0.033	0.085	0.044	0.028	0.014	0.063
Sum	0.125	0.240	0.222	0.151	0.269	0.228	0.152	0.064	0.042	0.133	0.141	0.146	0.126	0.336	0.064	0.095
Sum_All Congeners	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Homolog Groups (ng/kg)																
Dioxins																
TOTAL TETRA-DIOXINS	0.287	0.189	0.147	0.284	0.088	0.223	0.256	0.171	0.065	0.183	0.210	0.054	0.211	0.054	0.169	0.121
TOTAL PENTA-DIOXINS	0.252	0.200	0.131	0.241	0.081	0.209	0.235	0.130	0.060	0.184	0.175	0.055	0.200	0.065	0.155	0.094
TOTAL HEXA-DIOXINS	0.216	0.196	0.140	0.197	0.094	0.188	0.235	0.140	0.083	0.192	0.191	0.080	0.199	0.081	0.164	0.098
TOTAL HEPTA-DIOXINS	0.060	0.075	0.102	0.066	0.098	0.071	0.068	0.089	0.133	0.093	0.084	0.107	0.088	0.033	0.078	0.110
OCDD	0.078	0.120	0.245	0.079	0.334	0.109	0.062	0.332	0.562	0.144	0.141	0.413	0.147	0.036	0.286	0.426
Sum	0.893	0.779	0.765	0.866	0.695	0.800	0.856	0.863	0.902	0.796	0.801	0.710	0.845	0.269	0.852	0.849
Furans																
TOTAL TETRA-FURANS	0.056	0.082	0.065	0.074	0.055	0.089	0.080	0.067	0.021	0.105	0.108	0.058	0.075	0.131	0.078	0.048
TOTAL PENTA-FURANS	0.025	0.053	0.035	0.029	0.030	0.043	0.038	0.032	0.015	0.052	0.048	0.080	0.039	0.383	0.039	0.026
TOTAL HEXA-FURANS	0.013	0.042	0.033	0.015	0.022	0.020	0.016	0.015	0.024	0.026	0.022	0.051	0.018	0.199	0.017	0.016
TOTAL HEPTA-FURANS	0.009	0.031	0.056	0.009	0.079	0.022	0.007	0.013	0.026	0.014	0.012	0.052	0.012	0.015	0.009	0.024
OCDF	0.005	0.013	0.047	0.006	0.118	0.026	0.003	0.011	0.013	0.006	0.008	0.049	0.011	0.003	0.005	0.037
Sum	0.107	0.221	0.235	0.134	0.305	0.200	0.144	0.137	0.098	0.204	0.199	0.290	0.155	0.731	0.148	0.151
Sum_All Homologs	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Key:

J = Concentration is estimated.

U = Analyte was not detected.

Table 6-2. Normalized congeners and homolog results.

	FF01SS	FF02SS	FF03SS	FF04SS	FF05SS	FF06SS	FF07SS	FF08SS	FF09SS	RD01SS	RD02SS	T101SS	T103SS	T104SS	T201SS	T202SS
Congeners (ng/kg)																
Dioxins																
2,3,7,8-TCDD	0.004	0.009	0.011	0.010	0.006	0.010	0.009	0.009	0.012	0.001	0.004	0.002	0.005	0.001	0.005	0.003
1,2,3,7,8-PECDD	0.011	0.024	0.030	0.028	0.020	0.028	0.026	0.027	0.035	0.002	0.002	0.005	0.016	0.003	0.017	0.009 J
1,2,3,4,7,8-HXCDD	0.010	0.025	0.032	0.027	0.021	0.028	0.022	0.028	0.036	0.003	0.002	0.006	0.014	0.003	0.016	0.009 J
1,2,3,6,7,8-HXCDD	0.020	0.038	0.047	0.041	0.033	0.045	0.037	0.044	0.052	0.009	0.006	0.015	0.027	0.012	0.034	0.023
1,2,3,7,8,9-HXCDD	0.028	0.040	0.053	0.034	0.038	0.049	0.043	0.045	0.061	0.006	0.006	0.015	0.035	0.008	0.037	0.027
1,2,3,4,6,7,8-HPCDD	0.162	0.222	0.236	0.212	0.201	0.214	0.206	0.227	0.243	0.128	0.096	0.130	0.180	0.125	0.185	0.165
OCDD	0.643	0.429	0.384	0.420	0.525	0.420	0.466	0.413	0.324	0.788	0.827	0.668	0.585	0.679	0.557	0.637
Sum	0.877	0.787	0.794	0.772	0.844	0.794	0.809	0.794	0.762	0.937	0.944	0.841	0.863	0.831	0.850	0.874
Furans																
2,3,7,8-TCDF	0.013	0.049	0.041	0.053	0.024	0.043	0.047	0.047	0.059	0.001	0.001 U	0.006	0.026	0.002	0.029	0.008
1,2,3,7,8-PECDF	0.008	0.026	0.026	0.026	0.016	0.025	0.022	0.025	0.032	0.001	0.001 J	0.004	0.014	0.002 J	0.015	0.006 J
2,3,4,7,8-PECDF	0.010	0.034	0.031	0.032	0.018	0.029	0.027	0.030	0.040	0.001	0.002	0.006	0.019	0.002	0.019	0.009 J
1,2,3,4,7,8-HXCDF	0.006	0.016	0.017	0.013	0.011	0.013	0.013	0.016	0.018	0.002	0.002	0.006 U	0.011	0.003	0.009 U	0.007 J
1,2,3,6,7,8-HXCDF	0.006	0.015	0.016	0.014	0.009	0.015	0.012	0.013	0.019	0.001	0.001	0.004	0.009 J	0.002	0.010	0.006 J
1,2,3,7,8,9-HXCDF	0.000 J	0.002 J	0.002 UJ	0.002 J	0.001 UJ	0.002	0.001 J	0.002 J	0.002	0.000 J	0.000 J	0.000 J	0.001 J	0.000 J	0.001 J	0.001 J
2,3,4,6,7,8-HXCDF	0.006	0.016	0.014	0.014	0.009	0.012	0.011	0.013	0.017	0.001	0.001	0.005	0.009 J	0.002	0.010	0.006 J
1,2,3,4,6,7,8-HPCDF	0.031	0.027	0.030	0.027	0.027	0.030	0.029	0.031	0.028	0.020	0.015	0.033	0.023	0.046	0.026	0.027
1,2,3,4,7,8,9-HPCDF	0.002	0.003 J	0.004 J	0.003	0.003 UJ	0.004	0.003	0.004 J	0.004	0.001	0.001 J	0.003 J	0.003 J	0.002	0.003 J	0.002 J
OCDF	0.042	0.025	0.023	0.043	0.038	0.033	0.026	0.027	0.019	0.034	0.031	0.092	0.022	0.106	0.027	0.054
Sum	0.123	0.213	0.206	0.228	0.156	0.206	0.191	0.206	0.238	0.063	0.056	0.159	0.137	0.169	0.150	0.126
Sum_All Congeners	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Homolog Groups (ng/kg)																
Dioxins																
TOTAL TETRA-DIOXINS	0.125	0.213	0.238	0.257	0.189	0.239	0.213	0.239	0.259	0.019	0.053	0.081	0.144	0.054	0.148	0.122
TOTAL PENTA-DIOXINS	0.118	0.205	0.221	0.214	0.208	0.204	0.187	0.210	0.203	0.026	0.050	0.085	0.146	0.051	0.149	0.104
TOTAL HEXA-DIOXINS	0.143	0.170	0.200	0.140	0.210	0.185	0.178	0.176	0.198	0.051	0.057	0.122	0.160	0.080	0.171	0.140
TOTAL HEPTA-DIOXINS	0.113	0.068	0.063	0.063	0.087	0.063	0.075	0.067	0.058	0.183	0.128	0.133	0.095	0.132	0.097	0.131
OCDD	0.265	0.077	0.058	0.073	0.127	0.069	0.093	0.069	0.043	0.594	0.594	0.366	0.172	0.435	0.160	0.265
Sum	0.763	0.734	0.780	0.746	0.820	0.759	0.746	0.761	0.761	0.872	0.882	0.787	0.716	0.752	0.725	0.762
Furans																
TOTAL TETRA-FURANS	0.095	0.139	0.124	0.146	0.092	0.140	0.145	0.140	0.144	0.010	0.026	0.061	0.159	0.034	0.151	0.089
TOTAL PENTA-FURANS	0.061	0.083	0.061	0.068	0.045	0.063	0.069	0.061	0.063	0.016	0.022	0.039	0.077	0.025	0.075	0.059
TOTAL HEXA-FURANS	0.038	0.031	0.023	0.023	0.021	0.023	0.023	0.024	0.023	0.034	0.020	0.024	0.030	0.035	0.028	0.039
TOTAL HEPTA-FURANS	0.026	0.009	0.008	0.009	0.012	0.010	0.011	0.010	0.007	0.042	0.027	0.039	0.012	0.084	0.014	0.029
OCDF	0.017	0.005	0.004	0.008	0.009	0.005	0.005	0.004	0.003	0.026	0.023	0.050	0.006	0.068	0.008	0.022
Sum	0.237	0.266	0.220	0.254	0.180	0.241	0.254	0.239	0.239	0.128	0.118	0.213	0.284	0.248	0.275	0.238
Sum_All Homologs	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Key:

J = Concentration is estimated.

U = Analyte was not detected.

Table 6-2. Normalized congeners and homolog results.

	T203SS	T301SS	T302SS	T303SS	W102SS	W103SS	W104SS	W105SS	W107SS	W108SS	W109SS	W196SS	W197SS	W198SS	W201SS	W202SS
Congeners (ng/kg)																
Dioxins																
2,3,7,8-TCDD	0.005	0.004	0.004 U	0.001 J	0.005	0.003	0.009	0.010	0.024	0.001	0.001	0.001	0.024	0.005	0.003	0.005
1,2,3,7,8-PECDD	0.016	0.014	0.011 UJ	0.004 J	0.008	0.010	0.018	0.017	0.008	0.005	0.005	0.006 J	0.006	0.013	0.008	0.002
1,2,3,4,7,8-HXCDD	0.014	0.011 J	0.010 J	0.006 J	0.009	0.010	0.020	0.018	0.009	0.005	0.005	0.007	0.005	0.013	0.008	0.003
1,2,3,6,7,8-HXCDD	0.033	0.025	0.024	0.018	0.017	0.019	0.034	0.030	0.016	0.009	0.012	0.017	0.011	0.023	0.015	0.005
1,2,3,7,8,9-HXCDD	0.037	0.027	0.024	0.014	0.017	0.021	0.039	0.032	0.016	0.009	0.010	0.015	0.010	0.024	0.017	0.005
1,2,3,4,6,7,8-HPCDD	0.182	0.157	0.162	0.171	0.138	0.144	0.203	0.176	0.143	0.070	0.116	0.156	0.117	0.148	0.130	0.061
OCDD	0.588	0.625	0.662	0.743	0.707	0.637	0.528	0.596	0.691	0.674	0.722	0.731	0.734	0.642	0.688	0.681
Sum	0.874	0.862	0.898	0.957	0.901	0.844	0.852	0.880	0.906	0.774	0.871	0.933	0.907	0.868	0.869	0.763
Furans																
2,3,7,8-TCDF	0.020 U	0.025	0.012	0.004	0.011	0.014	0.022	0.016	0.009	0.006	0.004	0.003 U	0.004	0.015	0.013	0.003
1,2,3,7,8-PECDF	0.012	0.013	0.006 J	0.003 J	0.006	0.008	0.012	0.009	0.005	0.003	0.002	0.002 J	0.002	0.008	0.007	0.002
2,3,4,7,8-PECDF	0.015	0.015	0.008 J	0.004 J	0.007	0.011	0.015	0.011	0.005	0.004	0.003	0.003 J	0.003	0.010	0.009	0.002
1,2,3,4,7,8-HXCDF	0.011	0.010 J	0.006 UJ	0.003 J	0.005	0.008	0.009	0.008	0.004	0.003	0.002	0.003 J	0.002	0.006	0.006	0.002
1,2,3,6,7,8-HXCDF	0.008 J	0.007 J	0.005 J	0.003 J	0.005	0.007	0.009	0.007	0.004	0.003	0.002	0.003 J	0.003	0.006	0.006	0.001
1,2,3,7,8,9-HXCDF	0.001 J	0.002 J	0.001 UJ	0.001 UJ	0.000 J	0.001 J	0.001 J	0.001 J	0.000 UJ	0.000 UJ	0.000 J	0.002 U	0.000 J	0.001 J	0.000 J	0.000 J
2,3,4,6,7,8-HXCDF	0.008 J	0.008 J	0.005 J	0.003 J	0.004	0.007	0.008	0.006	0.003	0.003	0.002	0.002 U	0.002	0.005	0.006	0.001
1,2,3,4,6,7,8-HPCDF	0.024	0.025	0.025	0.012	0.022	0.041	0.032	0.022	0.020	0.022	0.023	0.020 J	0.022	0.025	0.030	0.020
1,2,3,4,7,8,9-HPCDF	0.003 J	0.003 J	0.002 J	0.001 J	0.002	0.002	0.003	0.002	0.002	0.001	0.001	0.001 J	0.001	0.002	0.002	0.001
OCDF	0.025	0.030	0.034	0.010 J	0.038	0.058	0.038	0.037	0.042	0.180	0.088	0.026	0.052	0.055	0.053	0.204
Sum	0.126	0.138	0.102	0.043	0.099	0.156	0.148	0.120	0.094	0.226	0.129	0.067	0.093	0.132	0.131	0.237
Sum_All Congeners	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Homolog Groups (ng/kg)																
Dioxins																
TOTAL TETRA-DIOXINS	0.128	0.152	0.104	0.058	0.176	0.183	0.228	0.246	0.183	0.137	0.110	0.073	0.104	0.220	0.170	0.081
TOTAL PENTA-DIOXINS	0.129	0.135	0.113	0.069	0.151	0.154	0.211	0.228	0.148	0.119	0.105	0.085	0.102	0.186	0.141	0.075
TOTAL HEXA-DIOXINS	0.165	0.143	0.158	0.113	0.156	0.149	0.208	0.212	0.150	0.112	0.101	0.117	0.106	0.178	0.124	0.080
TOTAL HEPTA-DIOXINS	0.118	0.103	0.138	0.190	0.081	0.078	0.070	0.061	0.100	0.060	0.112	0.162	0.110	0.073	0.088	0.070
OCDD	0.193	0.208	0.298	0.455	0.264	0.209	0.113	0.125	0.275	0.334	0.397	0.431	0.400	0.180	0.259	0.449
Sum	0.734	0.740	0.811	0.885	0.827	0.774	0.829	0.872	0.856	0.763	0.825	0.868	0.821	0.837	0.783	0.756
Furans																
TOTAL TETRA-FURANS	0.145	0.139	0.087	0.038	0.079	0.094	0.083	0.060	0.060	0.063	0.043	0.040	0.046	0.075	0.095	0.034
TOTAL PENTA-FURANS	0.068	0.065	0.044	0.028	0.038	0.055	0.043	0.032	0.030	0.037	0.025	0.025	0.042	0.038	0.049	0.025
TOTAL HEXA-FURANS	0.029	0.029	0.020	0.026	0.022	0.032	0.023	0.017	0.018	0.023	0.020	0.025	0.028	0.019	0.028	0.018
TOTAL HEPTA-FURANS	0.015	0.017	0.023	0.016	0.020	0.026	0.014	0.011	0.019	0.026	0.038	0.027	0.034	0.017	0.026	0.034
OCDF	0.008	0.010	0.015	0.006 J	0.014	0.019	0.008	0.008	0.017	0.089	0.048	0.016	0.028	0.015	0.020	0.135
Sum	0.266	0.260	0.189	0.115	0.173	0.226	0.171	0.128	0.144	0.237	0.175	0.132	0.179	0.163	0.217	0.244
Sum_All Homologs	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Key:
J = Concentration is estimated.
U = Analyte was not detected.

Table 6-2. Normalized congeners and homolog results.

	W203SS	W204SS	W205SS	W206SS	W207SS	W208SS	W209SS	W210SS	W211SS	W212SS	W213SS	W214SS	W215SS	W216SS	W299SS	W301SS
Congeners (ng/kg)																
Dioxins																
2,3,7,8-TCDD	0.020	0.007	0.004	0.003	0.030	0.003	0.194	0.054	0.002	0.006	0.041	0.016	0.008	0.003	0.009	0.005
1,2,3,7,8-PECDD	0.003	0.020	0.005	0.006	0.011	0.007	0.004	0.015	0.006	0.003	0.006	0.002	0.011	0.001	0.024	0.017
1,2,3,4,7,8-HXCDD	0.003	0.019	0.005	0.007	0.012	0.007	0.004	0.014	0.007	0.003	0.004	0.002	0.011	0.001	0.022	0.014
1,2,3,6,7,8-HXCDD	0.007	0.033	0.015	0.016	0.022	0.014	0.010	0.025	0.014	0.010	0.012	0.006	0.020	0.005	0.039	0.026
1,2,3,7,8,9-HXCDD	0.007	0.036	0.014	0.015	0.023	0.014	0.010	0.027	0.015	0.008	0.009	0.004	0.021	0.004	0.042	0.029
1,2,3,4,6,7,8-HPCDD	0.103	0.196	0.150	0.162	0.158	0.134	0.100	0.162	0.140	0.122	0.107	0.102	0.155	0.090	0.194	0.151
OCDD	0.752	0.525	0.614	0.690	0.617	0.686	0.572	0.565	0.725	0.767	0.740	0.668	0.671	0.842	0.503	0.603
Sum	0.894	0.835	0.807	0.900	0.874	0.866	0.894	0.862	0.910	0.919	0.919	0.801	0.897	0.947	0.832	0.845
Furans																
2,3,7,8-TCDF	0.003	0.024	0.006	0.005	0.014	0.008	0.005	0.015	0.005	0.003	0.007	0.002	0.013	0.002	0.035	0.022
1,2,3,7,8-PECDF	0.002	0.012	0.003	0.003	0.008	0.004	0.003	0.009	0.003 J	0.002	0.004	0.001	0.006	0.001	0.019	0.012
2,3,4,7,8-PECDF	0.002	0.016	0.004	0.005	0.010	0.006	0.004	0.011	0.004 J	0.002	0.005	0.001	0.008	0.001	0.024	0.016
1,2,3,4,7,8-HXCDF	0.002	0.010	0.004	0.004	0.006	0.004	0.004	0.007	0.004 UJ	0.002	0.003	0.002	0.006	0.002	0.011	0.009
1,2,3,6,7,8-HXCDF	0.001	0.009	0.004	0.004	0.006	0.004	0.004	0.007	0.003 J	0.002	0.003	0.002	0.005	0.001	0.011	0.008
1,2,3,7,8,9-HXCDF	0.000 J	0.001 J	0.000 J	0.000 J	0.001 J	0.000 J	0.000 J	0.001 J	0.000 J	0.000 UJ	0.000 J	0.000 J	0.001 UJ	0.000 J	0.001 J	0.001 J
2,3,4,6,7,8-HXCDF	0.002	0.009	0.004	0.004	0.005	0.003	0.005	0.006	0.003 J	0.002	0.002	0.001	0.004	0.001	0.010	0.008
1,2,3,4,6,7,8-HPCDF	0.017	0.033	0.087	0.027	0.028	0.027	0.028	0.035	0.024	0.027	0.018	0.049	0.021	0.012	0.025	0.031
1,2,3,4,7,8,9-HPCDF	0.001	0.003	0.002	0.001	0.002	0.002	0.002	0.002	0.002 J	0.001	0.001	0.002	0.002 J	0.001	0.003	0.003
OCDF	0.076	0.049	0.080	0.047	0.044	0.076	0.051	0.045	0.041	0.039	0.039	0.139	0.037	0.032	0.029	0.044
Sum	0.106	0.165	0.193	0.100	0.126	0.134	0.106	0.138	0.090	0.081	0.081	0.199	0.103	0.053	0.168	0.155
Sum_All Congeners	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Homolog Groups (ng/kg)																
Dioxins																
TOTAL TETRA-DIOXINS	0.077	0.241	0.110	0.148	0.188	0.176	0.188	0.227	0.089	0.087	0.116	0.064	0.191	0.026	0.211	0.199
TOTAL PENTA-DIOXINS	0.069	0.200	0.102	0.134	0.168	0.131	0.077	0.192	0.088	0.085	0.101	0.052	0.176	0.025	0.185	0.171
TOTAL HEXA-DIOXINS	0.081	0.196	0.121	0.146	0.174	0.143	0.101	0.182	0.123	0.115	0.102	0.061	0.155	0.042	0.193	0.158
TOTAL HEPTA-DIOXINS	0.124	0.070	0.122	0.117	0.092	0.086	0.101	0.078	0.147	0.128	0.104	0.113	0.092	0.127	0.073	0.073
OCDD	0.494	0.108	0.276	0.304	0.193	0.283	0.319	0.152	0.392	0.454	0.407	0.454	0.224	0.679	0.098	0.172
Sum	0.845	0.815	0.731	0.849	0.814	0.820	0.787	0.830	0.840	0.868	0.831	0.744	0.838	0.899	0.759	0.773
Furans																
TOTAL TETRA-FURANS	0.033	0.092	0.043	0.049	0.082	0.060	0.049	0.073	0.054	0.031	0.060	0.021	0.078	0.021	0.137	0.116
TOTAL PENTA-FURANS	0.024	0.044	0.025	0.033	0.043	0.036	0.056	0.041	0.031	0.021	0.038	0.014	0.038	0.013	0.064	0.052
TOTAL HEXA-FURANS	0.017	0.023	0.056	0.025	0.026	0.022	0.045	0.024	0.021	0.021	0.025	0.030	0.018	0.014	0.023	0.027
TOTAL HEPTA-FURANS	0.032	0.014	0.110	0.024	0.021	0.030	0.035	0.019	0.032	0.037	0.026	0.096	0.015	0.028	0.011	0.018
OCDF	0.050	0.010	0.036	0.021	0.014	0.031	0.028	0.012	0.022	0.023	0.021	0.094	0.012	0.026	0.006	0.013
Sum	0.155	0.185	0.269	0.151	0.186	0.180	0.213	0.170	0.160	0.132	0.169	0.256	0.162	0.101	0.241	0.227
Sum_All Homologs	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Key:

J = Concentration is estimated.

U = Analyte was not detected.

Table 6-2. Normalized congeners and homolog results.

	W302SS	W303SS	W304SS	W305SS	W306SS
Congeners (ng/kg)					
Dioxins					
2,3,7,8-TCDD	0.006	0.006	0.010	0.002	0.010
1,2,3,7,8-PECDD	0.010	0.015	0.003	0.003	0.006
1,2,3,4,7,8-HXCDD	0.010	0.014	0.003	0.003	0.007
1,2,3,6,7,8-HXCDD	0.018	0.026	0.008	0.007	0.012
1,2,3,7,8,9-HXCDD	0.024	0.028	0.007	0.006	0.013
1,2,3,4,6,7,8-HPCDD	0.133	0.167	0.115	0.098	0.116
OCDD	0.639	0.586	0.794	0.770	0.720
Sum	0.840	0.842	0.939	0.890	0.885
Furans					
2,3,7,8-TCDF	0.022	0.019	0.003	0.004	0.008
1,2,3,7,8-PECDF	0.007	0.012	0.002	0.002	0.005
2,3,4,7,8-PECDF	0.013	0.013	0.003	0.003	0.007
1,2,3,4,7,8-HXCDF	0.009	0.007	0.002	0.002	0.005
1,2,3,6,7,8-HXCDF	0.006	0.008	0.002	0.002	0.004
1,2,3,7,8,9-HXCDF	0.000 J	0.001 J	0.000 J	0.000 J	0.000 J
2,3,4,6,7,8-HXCDF	0.005	0.007	0.002	0.002	0.005
1,2,3,4,6,7,8-HPCDF	0.030	0.034	0.013	0.022	0.027
1,2,3,4,7,8,9-HPCDF	0.002	0.003	0.001	0.002	0.002
OCDF	0.065	0.054	0.034	0.071	0.051
Sum	0.160	0.158	0.061	0.110	0.115
Sum_All Congeners	1.0	1.0	1.0	1.0	1.0
Homolog Groups (ng/kg)					
Dioxins					
TOTAL TETRA-DIOXINS	0.157	0.201	0.090	0.087	0.148
TOTAL PENTA-DIOXINS	0.116	0.183	0.081	0.081	0.117
TOTAL HEXA-DIOXINS	0.121	0.173	0.094	0.082	0.125
TOTAL HEPTA-DIOXINS	0.084	0.080	0.117	0.099	0.090
OCDD	0.224	0.159	0.499	0.478	0.316
Sum	0.702	0.796	0.880	0.828	0.797
Furans					
TOTAL TETRA-FURANS	0.143	0.095	0.037	0.046	0.078
TOTAL PENTA-FURANS	0.077	0.049	0.022	0.025	0.047
TOTAL HEXA-FURANS	0.030	0.025	0.016	0.018	0.029
TOTAL HEPTA-FURANS	0.025	0.020	0.024	0.039	0.028
OCDF	0.023	0.015	0.021	0.044	0.022
Sum	0.298	0.204	0.120	0.172	0.203
Sum_All Homologs	1.0	1.0	1.0	1.0	1.0

Key:

J = Concentration is estimated.

U = Analyte was not detected.

Table 6-3. Dioxin/furan results as TEF-adjusted concentrations and TEQs.

	TEFs	E102SS	E103SS	E105SS	E106SS	E108SS	E109SS	E110SS	E111SS	E112SS	E116SS	E117SS	E121SS	E122SS	E194SS	E195SS	E196SS
Congeners (ng/kg)																	
Dioxins																	
2,3,7,8-TCDD	1	4.81	5.98	1.56	2.68	1.49	3.26	0.414	1.6	1.8	0.726	0.99	0.422	4.46	0.823	0.948	0.334
1,2,3,7,8-PECDD	1	5.44	4.71	5.91	6.51	5.1	10.6	1.52	5.21	7.02	2.69	4.64	1.26	2.67	2.62	3.59	1.04
1,2,3,4,7,8-HXCDD	0.1	0.525	0.537	0.783	0.684	0.552	1.25	0.152	0.613	0.905	0.297	0.546	0.143	0.307	0.269	0.4	0.111
1,2,3,6,7,8-HXCDD	0.1	0.829	0.959	1.21	1.29	1.22	1.99	0.389	0.96	1.37	0.462	0.929	0.255	0.559	0.432	0.755	0.183
1,2,3,7,8,9-HXCDD	0.1	0.937	0.978	1.3	1.35	1.14	2.09	0.331	1.11	1.53	0.494	1.01	0.248	0.558	0.467	0.835	0.213
1,2,3,4,6,7,8-HPCDD	0.01	0.513	0.93	0.769	1.04	1.28	1.17	0.379	0.568	1.2	0.262	0.552	0.251	0.426	0.199	1.07	0.166
OCDD	0.0003	0.0417	0.1014	0.06	0.1365	0.2049	0.09	0.0675	0.0384	0.384	0.01905	0.0453	0.0384	0.0642	0.01503	0.2298	0.039
Sum		13.10	14.20	11.59	13.69	10.99	20.45	3.25	10.10	14.21	4.95	8.71	2.62	9.04	4.83	7.83	2.09
Furans																	
2,3,7,8-TCDF	0.1	0.422	0.488	0.518	0.675	0.474	1.19	0.143	0.65	0.799	0.297	0.424	0.136	0.266	0.234	0.335	0.0702
1,2,3,7,8-PECDF	0.03	0.0819	0.0849	0.1092	0.1227	0.0903	0.2226	0.0273	0.1047	0.1428	0.0522	0.0867	0.02586	0.0528	0.0429 U	0.0567	0.01614
2,3,4,7,8-PECDF	0.3	0.969	1.008	1.233	1.656	1.116	2.682	0.36	1.248	1.776	0.609	1.035	0.327	0.633	0.522	0.708	0.1995
1,2,3,4,7,8-HXCDF	0.1	0.176	0.24	0.272	0.386	0.286	0.599	0.103	0.272 U	0.411	0.137	0.241	0.0914	0.131	0.117	0.164	0.0471 J
1,2,3,6,7,8-HXCDF	0.1	0.187	0.175	0.245	0.402	0.259	0.5	0.0843	0.242	0.362	0.107	0.193	0.0664	0.129	0.0924	0.138	0.0435 J
1,2,3,7,8,9-HXCDF	0.1	0.0204 J	0.0232 J	0.0273 J	0.0271 J	0.026 J	0.0527	0.007 UJ	0.0248 J	0.0353 J	0.0149 J	0.0243 J	0.0093 J	0.0168 J	0.0151 J	0.0163 J	0.0061 J
2,3,4,6,7,8-HXCDF	0.1	0.153	0.164	0.211	0.414	0.251	0.414	0.0859	0.195	0.321	0.0987	0.165	0.0648	0.111	0.0865	0.124	0.0384 J
1,2,3,4,6,7,8-HPCDF	0.01	0.0697	0.0826	0.075	0.308	0.237	0.123	0.0786	0.0552	0.0976	0.0279	0.0591	0.0509	0.0601	0.0217	0.0626	0.0259
1,2,3,4,7,8,9-HPCDF	0.01	0.00559	0.00744	0.00804	0.025	0.0172	0.0146 U	0.00397 J	0.00636	0.0107	0.00315 J	0.00623	0.00374 J	0.00501	0.00243 J	0.00548	0.00242 J
OCDF	0.0003	0.0033	0.00468	0.002751	0.02991	0.01743	0.00414	0.00357	0.002118	0.00402	0.000948	0.002439	0.00303	0.00384	0.000753	0.002709	0.002736
Sum		2.09	2.28	2.70	4.05	2.77	5.80	0.90	2.80	3.96	1.35	2.24	0.78	1.41	1.13	1.61	0.45
Total 2,3,7,8-TCDD TEQ (ng/kg)																	
ND=DL		15.2	16.5	14.3	17.7	13.8	26.3	4.15	12.9	18.2	6.30	10.9	3.40	10.5	5.96	9.44	2.54
ND=0		15.2	16.5	14.3	17.7	13.8	26.2	4.14	12.6	18.2	6.30	10.9	3.40	10.5	5.92	9.44	2.54
ND=0.5*DL		15.2	16.5	14.3	17.7	13.8	26.2	4.15	12.8	18.2	6.30	10.9	3.40	10.5	5.94	9.44	2.54

Key:
DL = Sample-specific detection limit.
J = Concentration is estimated.
ND = Nondetect.
TEF = Toxicity equivalency factor.
TEQ = Total toxic equivalent concentration.
U = Analyte was not detected.

Table 6-3. Dioxin/furan results as TEF-adjusted concentrations and TEQs.

	E197SS	E198SS	E199SS	E201SS	E204SS	E206SS	E208SS	E298SS	E299SS	E302SS	E402SS	E403SS	E405SS	E406SS	E498SS	E499SS
Congeners																
Dioxins																
2,3,7,8-TCDD	11.9	1.19	1.18	1.69	0.815	1.11	0.389 U	0.943	0.519	0.561	0.484	5.37	2.87	0.392	1.02	16.7
1,2,3,7,8-PECDD	7.1	4.62	2.46	6.31	1.71	3.78	1.69	2.88	2.34	1.64	1.58	12.9	2.11	2.14	2.89	1.21
1,2,3,4,7,8-HXCDD	0.854	0.591	0.24	0.763	0.169	0.398	0.204	0.321	0.357	0.159	0.171	1.19	0.236	0.153	0.311	0.14
1,2,3,6,7,8-HXCDD	1.33	0.943	0.445	1.14	0.369	0.629	0.314	0.665	1.1	0.299	0.322	3.61	0.472	0.429	0.62	0.284
1,2,3,7,8,9-HXCDD	1.57	1.2	0.523	1.2	0.305	0.711	0.358	0.625	0.726	0.317	0.335	3.16	0.48	0.346	0.595	0.269
1,2,3,4,6,7,8-HPCDD	0.752	0.646	0.358	0.688	0.438	0.371	0.171	0.576	1.45	0.175	0.17	3.31	0.277	0.141	0.401	0.367
OCDD	0.0519	0.0561	0.0465	0.0423	0.0756	0.02907	0.00804	0.1161	0.3	0.01524	0.01626	0.669	0.02601	0.00936	0.0816	0.0753
Sum	23.56	9.25	5.25	11.83	3.88	7.03	3.13	6.13	6.79	3.17	3.08	30.21	6.47	3.61	5.92	19.05
Furans																
2,3,7,8-TCDF	0.689	0.596	0.205	0.702	0.239	0.483	0.201	0.343	0.185	0.23	0.223	1.17	0.255	0.177	0.346	0.186
1,2,3,7,8-PECDF	0.1059	0.1485	0.0396	0.126	0.0399	0.0768	0.0351	0.0609	0.0375	0.0336	0.0378	0.2082	0.0432	0.0378	0.0681	0.0288
2,3,4,7,8-PECDF	1.362	2.034	0.474	1.524	0.462	0.984	0.411	0.831	0.486	0.444	0.441	3.6	0.531	1.242	0.84	0.369
1,2,3,4,7,8-HXCDF	0.284	0.61	0.168	0.277	0.131 U	0.179	0.0824	0.144	0.19	0.0729	0.0837	1.58	0.101	0.233	0.167	0.0779
1,2,3,6,7,8-HXCDF	0.278	0.562	0.12	0.28	0.0925	0.175	0.0722	0.15	0.23	0.0832	0.0909	1.16	0.097	0.491	0.149	0.0655
1,2,3,7,8,9-HXCDF	0.0298 J	0.0398 J	0.0109 J	0.0313 J	0.0111 J	0.02 J	0.0099 J	0.0175 J	0.0167 J	0.0119 J	0.000385 UJ	0.0621	0.0115 J	0.0085 J	0.018 J	0.0074 J
2,3,4,6,7,8-HXCDF	0.221	0.744	0.119	0.233	0.0817	0.154	0.0725	0.132	0.164	0.07	0.0772	1.21	0.088	0.591	0.135	0.0614
1,2,3,4,6,7,8-HPCDF	0.0826	0.296	0.196	0.0788	0.135	0.0652	0.0155	0.0543	0.175	0.0238	0.0241	1.12	0.0336	0.0553	0.0395	0.0463
1,2,3,4,7,8,9-HPCDF	0.00763	0.0236	0.00632	0.00844	0.0192	0.00677	0.00198 J	0.00551	0.011	0.00242 J	0.00271 J	0.0588	0.00336 UJ	0.00528	0.0046 J	0.00381 J
OCDF	0.00345	0.00627	0.00882	0.0033	0.02673	0.00693	0.000339	0.0039	0.00675	0.000618	0.000939	0.0798	0.001968	0.000726	0.001491	0.00651
Sum	3.06	5.06	1.35	3.26	1.24	2.15	0.90	1.74	1.50	0.97	0.99	10.25	1.17	2.84	1.77	0.85
Total 2,3,7,8-TCDD TEQ																
ND=DL	26.6	14.3	6.60	15.1	5.12	9.18	4.04	7.87	8.29	4.14	4.07	40.5	7.64	6.45	7.69	19.9
ND=0	26.6	14.3	6.60	15.1	4.99	9.18	3.65	7.87	8.29	4.14	4.06	40.5	7.63	6.45	7.69	19.9
ND=0.5*DL	26.6	14.3	6.60	15.1	5.05	9.18	3.84	7.87	8.29	4.14	4.06	40.5	7.63	6.45	7.69	19.9

Key:
DL = Sample-specific detection limit.
J = Concentration is estimated.
ND = Nondetect.
TEF = Toxicity equivalency factor.
TEQ = Total toxic equivalent concentration.
U = Analyte was not detected.

Table 6-3. Dioxin/furan results as TEF-adjusted concentrations and TEQs.

	FF01SS	FF02SS	FF03SS	FF04SS	FF05SS	FF06SS	FF07SS	FF08SS	FF09SS	RD01SS	RD02SS	T101SS	T103SS	T104SS	T201SS	T202SS	T203SS
Congeners																	
Dioxins																	
2,3,7,8-TCDD	3.43	1.2	1.18	2.61	0.485	3.54	2.03	0.86	4.56	0.564	1.64	0.187	0.249	0.197	0.634	0.156	0.315
1,2,3,7,8-PECDD	10.4	3.31	3.1	7.34	1.66	10.2	5.96	2.49	13.5	2	0.926	0.601	0.83	0.67	2.11	0.463 J	0.926
1,2,3,4,7,8-HXCDD	0.891	0.336	0.325	0.698	0.174	1.01	0.51	0.259	1.37	0.228	0.0878	0.0677	0.0738	0.0733	0.194	0.0453 J	0.0815
1,2,3,6,7,8-HXCDD	1.84	0.516	0.486	1.06	0.27	1.64	0.863	0.401	2	0.823	0.243	0.165	0.138	0.314	0.421	0.111	0.192
1,2,3,7,8,9-HXCDD	2.65	0.547	0.545	0.876	0.312	1.76	1	0.415	2.32	0.556	0.218	0.172	0.178	0.208	0.453	0.135	0.215
1,2,3,4,6,7,8-HPCDD	1.52	0.302	0.243	0.551	0.165	0.776	0.477	0.208	0.933	1.13	0.362	0.145	0.0925	0.314	0.228	0.0813	0.107
OCDD	0.1809	0.01749	0.01185	0.0327	0.01296	0.0456	0.0324	0.01134	0.0372	0.2079	0.0939	0.02232	0.009	0.0513	0.02064	0.00939	0.01038
Sum	20.91	6.23	5.89	13.17	3.08	18.97	10.87	4.64	24.72	5.51	3.57	1.36	1.57	1.83	4.06	1.00	1.85
Furans																	
2,3,7,8-TCDF	1.21	0.668	0.426	1.37	0.2	1.56	1.1	0.431	2.27	0.0543	0.0564 U	0.0719	0.133	0.0593	0.36	0.0395	0.115 U
1,2,3,7,8-PECDF	0.2112	0.1053	0.0804	0.2007	0.039	0.2727	0.1512	0.0687	0.363	0.02199	0.01311 J	0.01425	0.02172	0.01188 J	0.0555	0.00858 J	0.02094
2,3,4,7,8-PECDF	2.796	1.395	0.957	2.457	0.432	3.12	1.905	0.837	4.56	0.2691	0.192	0.1893	0.2997	0.1782	0.717	0.1332 J	0.2652
1,2,3,4,7,8-HXCDF	0.567	0.22	0.178	0.35	0.0915	0.475	0.305	0.143	0.686	0.193	0.0624	0.0691 U	0.0567	0.0654	0.113 U	0.0335 J	0.0649
1,2,3,6,7,8-HXCDF	0.533	0.201	0.169	0.371	0.0759	0.553	0.27	0.12	0.713	0.116	0.0524	0.0482	0.0458 J	0.0543	0.122	0.0293 J	0.0452 J
1,2,3,7,8,9-HXCDF	0.0465 J	0.0214 J	0.023 UJ	0.0438 J	0.0098 UJ	0.063	0.0288 J	0.0162 J	0.0844	0.0221 J	0.0076 J	0.0042 J	0.0045 J	0.005 J	0.0105 J	0.0027 J	0.0047 J
2,3,4,6,7,8-HXCDF	0.533	0.215	0.139	0.364	0.0714	0.442	0.253	0.115	0.643	0.117	0.0541	0.0519	0.047 J	0.0599	0.123	0.0316 J	0.0475 J
1,2,3,4,6,7,8-HPCDF	0.292	0.0361	0.0308	0.0713	0.0219	0.109	0.0667	0.028	0.109	0.175	0.0558	0.0366	0.0116	0.117	0.0326	0.0134	0.0143
1,2,3,4,7,8,9-HPCDF	0.0169	0.00468 J	0.00437 J	0.00891	0.00275 UJ	0.013	0.00695	0.00332 J	0.0164	0.0104	0.00392 J	0.00286 J	0.00157 J	0.00629	0.00353 J	0.00118 J	0.00166 J
OCDF	0.01173	0.001035	0.000714	0.00336	0.000945	0.00363	0.001815	0.000729	0.002169	0.009	0.00357	0.00306	0.000339	0.00804	0.001011	0.000792	0.000441
Sum	6.22	2.87	2.01	5.24	0.95	6.61	4.09	1.76	9.45	0.99	0.50	0.49	0.62	0.57	1.54	0.29	0.58
Total 2,3,7,8-TCDD TEQ																	
ND=DL	27.1	9.10	7.90	18.4	4.02	25.6	15.0	6.41	34.2	6.50	4.07	1.85	2.19	2.39	5.60	1.29	2.43
ND=0	27.1	9.10	7.88	18.4	4.01	25.6	15.0	6.41	34.2	6.50	4.02	1.78	2.19	2.39	5.49	1.29	2.31
ND=0.5*DL	27.1	9.10	7.89	18.4	4.02	25.6	15.0	6.41	34.2	6.50	4.04	1.82	2.19	2.39	5.54	1.29	2.37

Key:
DL = Sample-specific detection limit.
J = Concentration is estimated.
ND = Nondetect.
TEF = Toxicity equivalency factor.
TEQ = Total toxic equivalent concentration.
U = Analyte was not detected.

Table 6-3. Dioxin/furan results as TEF-adjusted concentrations and TEQs.

	T301SS	T302SS	T303SS	W102SS	W103SS	W104SS	W105SS	W107SS	W108SS	W109SS	W196SS	W197SS	W198SS	W201SS	W202SS	W203SS
Congeners																
Dioxins																
2,3,7,8-TCDD	0.192	0.155 U	0.073 J	2.16	1.01	2.91	3.87	15	1.01	1.12	0.104	14.5	3.4	1.53	5.65	16.8
1,2,3,7,8-PECDD	0.632	0.439 UJ	0.384 J	3.73	2.98	5.68	6.58	5.12	3.16	3.56	0.438 J	3.72	8.69	4.06	2.79	2.48
1,2,3,4,7,8-HXCDD	0.0526 J	0.0403 J	0.0518 J	0.391	0.317	0.619	0.695	0.559	0.331	0.388	0.0544	0.281	0.924	0.395	0.303	0.237
1,2,3,6,7,8-HXCDD	0.114	0.093	0.156	0.728	0.599	1.04	1.12	0.995	0.626	0.932	0.126	0.689	1.58	0.762	0.615	0.602
1,2,3,7,8,9-HXCDD	0.123	0.0956	0.128	0.747	0.642	1.2	1.21	1.03	0.658	0.79	0.114	0.595	1.66	0.831	0.617	0.555
1,2,3,4,6,7,8-HPCDD	0.0719	0.0637	0.152	0.611	0.451	0.627	0.665	0.901	0.485	0.89	0.115	0.712	1.02	0.642	0.707	0.851
OCDD	0.00861	0.0078	0.01986	0.0936	0.0597	0.0489	0.0675	0.1308	0.1401	0.1665	0.0162	0.1341	0.1329	0.102	0.2361	0.1869
Sum	1.19	0.89	0.96	8.46	6.06	12.12	14.21	23.74	6.41	7.85	0.97	20.63	17.41	8.32	10.92	21.71
Furans																
2,3,7,8-TCDF	0.113	0.0456	0.0381	0.476	0.423	0.68	0.604	0.554	0.448	0.342	0.0238 U	0.239	1.01	0.622	0.329	0.256
1,2,3,7,8-PECDF	0.01743	0.00666 J	0.00738 J	0.0759	0.0756	0.1119	0.1032	0.0894	0.0648	0.057	0.0054 J	0.0456	0.1668	0.0999	0.0525	0.042
2,3,4,7,8-PECDF	0.2097	0.0888 J	0.0948 J	0.942	1.029	1.389	1.275	1.035	0.897	0.69	0.075 J	0.594	2.079	1.314	0.75	0.588
1,2,3,4,7,8-HXCDF	0.046 J	0.0247 UJ	0.028 J	0.212	0.257	0.282	0.294	0.257	0.206	0.175	0.0231 J	0.148	0.417	0.277	0.209	0.157
1,2,3,6,7,8-HXCDF	0.0324 J	0.0201 J	0.0267 J	0.216	0.203	0.275	0.278	0.224	0.189	0.166	0.0193 J	0.161	0.394	0.278	0.161	0.124
1,2,3,7,8,9-HXCDF	0.008 J	0.0027 UJ	0.0075 UJ	0.0172 J	0.0176 J	0.0284 J	0.0277 J	0.0223 UJ	0.0144 UJ	0.0173 J	0.00238 U	0.0127 J	0.0379 J	0.0244 J	0.0129 J	0.0111 J
2,3,4,6,7,8-HXCDF	0.0356 J	0.0197 J	0.0238 J	0.17	0.207	0.238	0.222	0.206	0.18	0.154	0.017 U	0.152	0.35	0.298	0.165	0.129
1,2,3,4,6,7,8-HPCDF	0.0116	0.00964	0.0104	0.096	0.129	0.0982	0.0845	0.127	0.153	0.179	0.0145 J	0.134	0.172	0.148	0.236	0.139
1,2,3,4,7,8,9-HPCDF	0.00154 J	0.00091 J	0.00113 J	0.00775	0.00696	0.00923	0.00811	0.0101	0.0101	0.011	0.00085 J	0.00904	0.0148	0.011	0.0135	0.00843
OCDF	0.000414	0.000396	0.000261 J	0.00498	0.0054	0.00348	0.00417	0.00789	0.0375	0.02031	0.000585	0.00954	0.01131	0.00786	0.0708	0.01878
Sum	0.48	0.22	0.24	2.22	2.35	3.12	2.90	2.53	2.20	1.81	0.20	1.50	4.65	3.08	2.00	1.47
Total 2,3,7,8-TCDD TEQ																
ND=DL	1.67	1.11	1.20	10.7	8.41	15.2	17.1	26.3	8.61	9.66	1.16	22.1	22.1	11.4	12.9	23.2
ND=0	1.67	0.49	1.20	10.7	8.41	15.2	17.1	26.2	8.60	9.66	1.09	22.1	22.1	11.4	12.9	23.2
ND=0.5*DL	1.67	0.80	1.20	10.7	8.41	15.2	17.1	26.3	8.60	9.66	1.13	22.1	22.1	11.4	12.9	23.2

Key:

DL = Sample-specific detection limit.

J = Concentration is estimated.

ND = Nondetect

TEF = Toxicity equivalency factor.

TEQ = Total toxic equivalent concentration.

U = Analyte was not detected.

Table 6-3. Dioxin/furan results as TEF-adjusted concentrations and TEQs.

	W204SS	W205SS	W206SS	W207SS	W208SS	W209SS	W210SS	W211SS	W212SS	W213SS	W214SS	W215SS	W216SS	W299SS	W301SS	W302SS
Congeners																
Dioxins																
2,3,7,8-TCDD	2.42	2.46	2.62	7.42	0.961	72	16.3	0.254	2.42	22	19.8	1.74	7.1	1.87	1.54	2.38
1,2,3,7,8-PECDD	7.14	2.64	4.29	2.8	2.14	1.64	4.39	0.661	1.23	2.99	2.68	2.35	2.86	4.72	4.88	4.2
1,2,3,4,7,8-HXCDD	0.693	0.306	0.514	0.284	0.215	0.163	0.425	0.0671	0.129	0.24	0.264	0.249	0.272	0.435	0.394	0.428
1,2,3,6,7,8-HXCDD	1.18	0.861	1.22	0.545	0.426	0.376	0.769	0.143	0.404	0.621	0.744	0.449	1.08	0.781	0.72	0.763
1,2,3,7,8,9-HXCDD	1.3	0.788	1.16	0.568	0.435	0.362	0.806	0.158	0.343	0.509	0.522	0.466	0.891	0.835	0.811	1
1,2,3,4,6,7,8-HPCDD	0.708	0.855	1.24	0.387	0.401	0.37	0.491	0.143	0.501	0.576	1.24	0.344	2.06	0.39	0.424	0.566
OCDD	0.057	0.105	0.1581	0.0453	0.0618	0.0636	0.0513	0.02223	0.0945	0.1194	0.2439	0.0447	0.576	0.0303	0.051	0.0813
Sum	13.50	8.02	11.20	12.05	4.64	74.97	23.23	1.45	5.12	27.06	25.49	5.64	14.84	9.06	8.82	9.42
Furans																
2,3,7,8-TCDF	0.867	0.319	0.419	0.345	0.239	0.177	0.45	0.0549	0.126	0.381	0.234	0.287	0.476	0.701	0.608	0.948
1,2,3,7,8-PECDF	0.1299	0.0477	0.0789	0.0585	0.0396	0.02901	0.0822	0.01038 J	0.02277	0.0576	0.0423	0.0417	0.0678	0.1155	0.1014	0.0897
2,3,4,7,8-PECDF	1.788	0.633	1.038	0.732	0.51	0.483	1.035	0.1326 J	0.2901	0.741	0.522	0.561	1.008	1.428	1.344	1.704
1,2,3,4,7,8-HXCDF	0.363	0.227	0.286	0.154	0.116	0.155	0.223	0.0368 UJ	0.093	0.153	0.252	0.125	0.377	0.226	0.264	0.375
1,2,3,6,7,8-HXCDF	0.33	0.206	0.286	0.149	0.12	0.145	0.209	0.0321 J	0.0744	0.14	0.201	0.112	0.178	0.226	0.237	0.241
1,2,3,7,8,9-HXCDF	0.0318 J	0.0188 J	0.0183 J	0.0159 J	0.0098 J	0.0115 J	0.0199 J	0.0033 J	0.0072 UJ	0.0112 J	0.0129 J	0.0136 UJ	0.015 J	0.0249 J	0.0231 J	0.0182 J
2,3,4,6,7,8-HXCDF	0.309	0.212	0.271	0.134	0.0974	0.169	0.196	0.0313 J	0.0724	0.131	0.169	0.0885	0.174	0.195	0.229	0.225
1,2,3,4,6,7,8-HPCDF	0.12	0.497	0.205	0.0696	0.0805	0.105	0.106	0.0247	0.112	0.0975	0.592	0.0458	0.278	0.0509	0.0887	0.127
1,2,3,4,7,8,9-HPCDF	0.00994	0.0141	0.0105	0.00577	0.00606	0.00683	0.00654	0.00191 J	0.00494	0.00627	0.0282	0.00448 J	0.0187	0.00511	0.00812	0.00987
OCDF	0.00528	0.01371	0.01083	0.00324	0.00684	0.00564	0.00405	0.00126	0.00483	0.00624	0.0507	0.002475	0.02202	0.001728	0.00375	0.00828
Sum	3.95	2.19	2.62	1.67	1.23	1.29	2.33	0.33	0.81	1.72	2.10	1.28	2.61	2.97	2.91	3.75
Total 2,3,7,8-TCDD TEQ																
ND=DL	17.5	10.2	13.8	13.7	5.87	76.3	25.6	1.78	5.93	28.8	27.6	6.92	17.5	12.0	11.7	13.2
ND=0	17.5	10.2	13.8	13.7	5.87	76.3	25.6	1.74	5.92	28.8	27.6	6.91	17.5	12.0	11.7	13.2
ND=0.5*DL	17.5	10.2	13.8	13.7	5.87	76.3	25.6	1.76	5.93	28.8	27.6	6.92	17.5	12.0	11.7	13.2

Key:
DL = Sample-specific detection limit.
J = Concentration is estimated.
ND = Nondetect.
TEF = Toxicity equivalency factor.
TEQ = Total toxic equivalent concentration.
U = Analyte was not detected.

Table 6-3. Dioxin/furan results as TEF-adjusted concentrations and TEQs.

	W303SS	W304SS	W305SS	W306SS
Congeners				
Dioxins				
2,3,7,8-TCDD	1.78	13	0.98	4.69
1,2,3,7,8-PECDD	4.36	4.09	1.42	2.89
1,2,3,4,7,8-HXCDD	0.392	0.429	0.135	0.315
1,2,3,6,7,8-HXCDD	0.745	1.04	0.295	0.582
1,2,3,7,8,9-HXCDD	0.808	0.896	0.275	0.629
1,2,3,4,6,7,8-HPCDD	0.483	1.53	0.418	0.548
OCDD	0.0507	0.318	0.0981	0.102
Sum	8.62	21.30	3.62	9.76
Furans				
2,3,7,8-TCDF	0.558	0.435	0.162	0.401
1,2,3,7,8-PECDF	0.102	0.0765	0.02928	0.0768
2,3,4,7,8-PECDF	1.146	1.014	0.393	0.957
1,2,3,4,7,8-HXCDF	0.216	0.27	0.0965	0.217
1,2,3,6,7,8-HXCDF	0.225	0.207	0.0724	0.212
1,2,3,7,8,9-HXCDF	0.0223 J	0.0205 J	0.0069 J	0.0194 J
2,3,4,6,7,8-HXCDF	0.212	0.214	0.0813	0.22
1,2,3,4,6,7,8-HPCDF	0.0977	0.168	0.0944	0.128
1,2,3,4,7,8,9-HPCDF	0.00867	0.0126	0.00649	0.0101
OCDF	0.00465	0.01368	0.009	0.00726
Sum	2.59	2.43	0.95	2.25
Total 2,3,7,8-TCDD TEQ				
ND=DL	11.2	23.7	4.57	12.0
ND=0	11.2	23.7	4.57	12.0
ND=0.5*DL	11.2	23.7	4.57	12.0

Key:
DL = Sample-specific detection limit.
J = Concentration is estimated.
ND = Nondetect.
TEF = Toxicity equivalency factor.
TEQ = Total toxic equivalent concentration.
U = Analyte was not detected.

Table 6-4. Normalized TEQ contributions by congener.

	E102SS	E103SS	E105SS	E106SS	E108SS	E109SS	E110SS	E111SS	E112SS	E116SS	E117SS	E121SS	E122SS	E194SS	E195SS	E196SS	E197SS
Congeners																	
Dioxins																	
2,3,7,8-TCDD	0.317	0.363	0.109	0.151	0.108	0.124	0.100	0.125	0.099	0.115	0.090	0.124	0.427	0.139	0.100	0.132	0.447
1,2,3,7,8-PECDD	0.358	0.286	0.413	0.367	0.371	0.404	0.367	0.408	0.386	0.427	0.424	0.371	0.255	0.441	0.380	0.410	0.267
1,2,3,4,7,8-HXCDD	0.035	0.033	0.055	0.039	0.040	0.048	0.037	0.048	0.050	0.047	0.050	0.042	0.029	0.045	0.042	0.044	0.032
1,2,3,6,7,8-HXCDD	0.055	0.058	0.085	0.073	0.089	0.076	0.094	0.075	0.075	0.073	0.085	0.075	0.053	0.073	0.080	0.072	0.050
1,2,3,7,8,9-HXCDD	0.062	0.059	0.091	0.076	0.083	0.080	0.080	0.087	0.084	0.078	0.092	0.073	0.053	0.079	0.088	0.084	0.059
1,2,3,4,6,7,8-HPCDD	0.034	0.056	0.054	0.059	0.093	0.045	0.091	0.045	0.066	0.042	0.050	0.074	0.041	0.034	0.113	0.065	0.028
OCDD	0.003	0.006	0.004	0.008	0.015	0.003	0.016	0.003	0.021	0.003	0.004	0.011	0.006	0.003	0.024	0.015	0.002
Sum	0.862	0.862	0.811	0.772	0.798	0.779	0.785	0.791	0.782	0.786	0.796	0.771	0.865	0.813	0.829	0.822	0.885
Furans																	
2,3,7,8-TCDF	0.02779	0.030	0.036	0.038	0.034	0.045	0.034	0.051	0.044	0.047	0.039	0.040	0.025	0.039	0.035	0.028	0.026
1,2,3,7,8-PECDF	0.00539	0.005	0.008	0.007	0.007	0.008	0.007	0.008	0.008	0.008	0.008	0.008	0.005	0.004 U	0.006	0.006	0.004
2,3,4,7,8-PECDF	0.06382	0.061	0.086	0.093	0.081	0.102	0.087	0.098	0.098	0.097	0.095	0.096	0.061	0.088	0.075	0.079	0.051
1,2,3,4,7,8-HXCDF	0.01159	0.015	0.019	0.022	0.021	0.023	0.025	0.011 U	0.023	0.022	0.022	0.027	0.013	0.020	0.017	0.019 J	0.011
1,2,3,6,7,8-HXCDF	0.01232	0.011	0.017	0.023	0.019	0.019	0.020	0.019	0.020	0.017	0.018	0.020	0.012	0.016	0.015	0.017 J	0.010
1,2,3,7,8,9-HXCDF	0.00134 J	0.001 J	0.002 J	0.002 J	0.002 J	0.002	0.001 UJ	0.002 J	0.002 J	0.002 J	0.002 J	0.003 J	0.002 J	0.003 J	0.002 J	0.002 J	0.001 J
2,3,4,6,7,8-HXCDF	0.01008	0.010	0.015	0.023	0.018	0.016	0.021	0.015	0.018	0.016	0.015	0.019	0.011	0.015	0.013	0.015 J	0.008
1,2,3,4,6,7,8-HPCDF	0.00459	0.005	0.005	0.017	0.017	0.005	0.019	0.004	0.005	0.004	0.005	0.015	0.006	0.004	0.007	0.010	0.003
1,2,3,4,7,8,9-HPCDF	0.00037	0.000	0.001	0.001	0.001	0.000 U	0.001 J	0.000	0.001	0.001 J	0.001	0.001 J	0.000	0.000 J	0.001	0.001 J	0.000
OCDF	0.00022	0.000	0.001	0.002	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.000
Sum	0.138	0.138	0.190	0.228	0.202	0.221	0.215	0.209	0.218	0.214	0.204	0.229	0.135	0.187	0.171	0.178	0.115
Total 2,3,7,8-TCDD TEQ																	
ND=0.5*DL	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Key:

DL = Sample-specific detection limit.

J = Concentration is estimated.

ND = Nondetect.

TEF = Toxicity equivalency factor.

TEQ = Total toxic equivalent concentration.

U = Analyte was not detected.

Table 6-4. Normalized TEQ contributions by congener.

	E198SS	E199SS	E201SS	E204SS	E206SS	E208SS	E298SS	E299SS	E302SS	E402SS	E403SS	E405SS	E406SS	E498SS	E499SS	FF01SS
Congeners																
Dioxins																
2,3,7,8-TCDD	0.083	0.179	0.112	0.161	0.121	0.051 U	0.120	0.063	0.136	0.119	0.133	0.376	0.061	0.133	0.839	0.126
1,2,3,7,8-PECDD	0.323	0.373	0.418	0.338	0.412	0.440	0.366	0.282	0.396	0.389	0.319	0.276	0.332	0.376	0.061	0.383
1,2,3,4,7,8-HXCDD	0.041	0.036	0.051	0.033	0.043	0.053	0.041	0.043	0.038	0.042	0.029	0.031	0.024	0.040	0.007	0.033
1,2,3,6,7,8-HXCDD	0.066	0.067	0.076	0.073	0.069	0.082	0.085	0.133	0.072	0.079	0.089	0.062	0.066	0.081	0.014	0.068
1,2,3,7,8,9-HXCDD	0.084	0.079	0.079	0.060	0.077	0.093	0.079	0.088	0.077	0.082	0.078	0.063	0.054	0.077	0.014	0.098
1,2,3,4,6,7,8-HPCDD	0.045	0.054	0.046	0.087	0.040	0.045	0.073	0.175	0.042	0.042	0.082	0.036	0.022	0.052	0.018	0.056
OCDD	0.004	0.007	0.003	0.015	0.003	0.002	0.015	0.036	0.004	0.004	0.017	0.003	0.001	0.011	0.004	0.007
Sum	0.646	0.796	0.784	0.768	0.766	0.765	0.779	0.819	0.765	0.758	0.747	0.848	0.560	0.770	0.957	0.771
Furans																
2,3,7,8-TCDF	0.042	0.031	0.046	0.047	0.053	0.052	0.044	0.022	0.056	0.055	0.029	0.033	0.027	0.045	0.009	0.045
1,2,3,7,8-PECDF	0.010	0.006	0.008	0.008	0.008	0.009	0.008	0.005	0.008	0.009	0.005	0.006	0.006	0.009	0.001	0.008
2,3,4,7,8-PECDF	0.142	0.072	0.101	0.091	0.107	0.107	0.106	0.059	0.107	0.109	0.089	0.070	0.192	0.109	0.019	0.103
1,2,3,4,7,8-HXCDF	0.043	0.025	0.018	0.013 U	0.020	0.021	0.018	0.023	0.018	0.021	0.039	0.013	0.036	0.022	0.004	0.021
1,2,3,6,7,8-HXCDF	0.039	0.018	0.019	0.018	0.019	0.019	0.019	0.028	0.020	0.022	0.029	0.013	0.076	0.019	0.003	0.020
1,2,3,7,8,9-HXCDF	0.003 J	0.002 J	0.002 J	0.002 J	0.002 J	0.003 J	0.002 J	0.002 J	0.003 J	0.000 U	0.002	0.002 J	0.001 J	0.002 J	0.000 J	0.002 J
2,3,4,6,7,8-HXCDF	0.052	0.018	0.015	0.016	0.017	0.019	0.017	0.020	0.017	0.019	0.030	0.012	0.092	0.018	0.003	0.020
1,2,3,4,6,7,8-HPCDF	0.021	0.030	0.005	0.027	0.007	0.004	0.007	0.021	0.006	0.006	0.028	0.004	0.009	0.005	0.002	0.011
1,2,3,4,7,8,9-HPCDF	0.002	0.001	0.001	0.004	0.001	0.001 J	0.001	0.001	0.001 J	0.001 J	0.001	0.000 UJ	0.001	0.001 J	0.000 J	0.001
OCDF	0.000	0.001	0.000	0.005	0.001	0.000	0.000	0.001	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000
Sum	0.354	0.204	0.216	0.232	0.234	0.235	0.221	0.181	0.235	0.242	0.253	0.152	0.440	0.230	0.043	0.229
Total 2,3,7,8-TCDD TEQ																
ND=0.5*DL	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Key:
DL = Sample-specific detection limit.
J = Concentration is estimated.
ND = Nondetect.
TEF = Toxicity equivalency factor.
TEQ = Total toxic equivalent concentration.
U = Analyte was not detected.

Table 6-4. Normalized TEQ contributions by congener.

	FF02SS	FF03SS	FF04SS	FF05SS	FF06SS	FF07SS	FF08SS	FF09SS	RD01SS	RD02SS	T101SS	T103SS	T104SS	T201SS	T202SS	T203SS
Congeners																
Dioxins																
2,3,7,8-TCDD	0.132	0.150	0.142	0.121	0.138	0.136	0.134	0.133	0.087	0.406	0.103	0.114	0.082	0.114	0.120	0.133
1,2,3,7,8-PECDD	0.364	0.393	0.399	0.413	0.399	0.398	0.389	0.395	0.308	0.229	0.331	0.379	0.280	0.381	0.358 J	0.391
1,2,3,4,7,8-HXCDD	0.037	0.041	0.038	0.043	0.039	0.034	0.040	0.040	0.035	0.022	0.037	0.034	0.031	0.035	0.035 J	0.034
1,2,3,6,7,8-HXCDD	0.057	0.062	0.058	0.067	0.064	0.058	0.063	0.059	0.127	0.060	0.091	0.063	0.131	0.076	0.086	0.081
1,2,3,7,8,9-HXCDD	0.060	0.069	0.048	0.078	0.069	0.067	0.065	0.068	0.086	0.054	0.095	0.081	0.087	0.082	0.104	0.091
1,2,3,4,6,7,8-HPCDD	0.033	0.031	0.030	0.041	0.030	0.032	0.032	0.027	0.174	0.090	0.080	0.042	0.131	0.041	0.063	0.045
OCDD	0.002	0.002	0.002	0.003	0.002	0.002	0.002	0.001	0.032	0.023	0.012	0.004	0.021	0.004	0.007	0.004
Sum	0.685	0.747	0.715	0.766	0.742	0.727	0.725	0.724	0.848	0.883	0.749	0.716	0.764	0.733	0.773	0.780
Furans																
2,3,7,8-TCDF	0.073	0.054	0.074	0.050	0.061	0.074	0.067	0.066	0.008	0.007 U	0.040	0.061	0.025	0.065	0.031	0.024 U
1,2,3,7,8-PECDF	0.012	0.010	0.011	0.010	0.011	0.010	0.011	0.011	0.003	0.003 J	0.008	0.010	0.005 J	0.010	0.007 J	0.009
2,3,4,7,8-PECDF	0.153	0.121	0.133	0.108	0.122	0.127	0.131	0.133	0.041	0.047	0.104	0.137	0.074	0.129	0.103 J	0.112
1,2,3,4,7,8-HXCDF	0.024	0.023	0.019	0.023	0.019	0.020	0.022	0.020	0.030	0.015	0.019 U	0.026	0.027	0.010 U	0.026 J	0.027
1,2,3,6,7,8-HXCDF	0.022	0.021	0.020	0.019	0.022	0.018	0.019	0.021	0.018	0.013	0.027	0.021 J	0.023	0.022	0.023 J	0.019 J
1,2,3,7,8,9-HXCDF	0.002 J	0.001 UJ	0.002 J	0.001 UJ	0.002	0.002 J	0.003 J	0.002	0.003 J	0.002 J	0.002 J	0.002 J	0.002 J	0.002 J	0.002 J	0.002 J
2,3,4,6,7,8-HXCDF	0.024	0.018	0.020	0.018	0.017	0.017	0.018	0.019	0.018	0.013	0.029	0.021 J	0.025	0.022	0.024 J	0.020 J
1,2,3,4,6,7,8-HPCDF	0.004	0.004	0.004	0.005	0.004	0.004	0.004	0.003	0.027	0.014	0.020	0.005	0.049	0.006	0.010	0.006
1,2,3,4,7,8,9-HPCDF	0.001 J	0.001 J	0.000	0.000 UJ	0.001	0.000	0.001 J	0.000	0.002	0.001 J	0.002 J	0.001 J	0.003	0.001 J	0.001 J	0.001 J
OCDF	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.002	0.000	0.003	0.000	0.001	0.000
Sum	0.315	0.253	0.285	0.234	0.258	0.273	0.275	0.276	0.152	0.117	0.251	0.284	0.236	0.267	0.227	0.220
Total 2,3,7,8-TCDD TEQ																
ND=0.5*DL	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Key:

DL = Sample-specific detection limit.

J = Concentration is estimated.

ND = Nondetect.

TEF = Toxicity equivalency factor.

TEQ = Total toxic equivalent concentration.

U = Analyte was not detected.

Table 6-4. Normalized TEQ contributions by congener.

	T301SS	T302SS	T303SS	W102SS	W103SS	W104SS	W105SS	W107SS	W108SS	W109SS	W196SS	W197SS	W198SS	W201SS	W202SS	W203SS
Congeners																
Dioxins																
2,3,7,8-TCDD	0.115	0.097 U	0.061 J	0.202	0.120	0.191	0.226	0.571	0.117	0.116	0.092	0.655	0.154	0.134	0.437	0.725
1,2,3,7,8-PECDD	0.378	0.273 UJ	0.320 J	0.349	0.354	0.373	0.385	0.195	0.367	0.369	0.388 J	0.168	0.394	0.356	0.216	0.107
1,2,3,4,7,8-HXCDD	0.032 J	0.050 J	0.043 J	0.037	0.038	0.041	0.041	0.021	0.038	0.040	0.048	0.013	0.042	0.035	0.023	0.010
1,2,3,6,7,8-HXCDD	0.068	0.116	0.130	0.068	0.071	0.068	0.065	0.038	0.073	0.096	0.112	0.031	0.072	0.067	0.048	0.026
1,2,3,7,8,9-HXCDD	0.074	0.119	0.107	0.070	0.076	0.079	0.071	0.039	0.076	0.082	0.101	0.027	0.075	0.073	0.048	0.024
1,2,3,4,6,7,8-HPCDD	0.043	0.079	0.127	0.057	0.054	0.041	0.039	0.034	0.056	0.092	0.102	0.032	0.046	0.056	0.055	0.037
OCDD	0.005	0.010	0.017	0.009	0.007	0.003	0.004	0.005	0.016	0.017	0.014	0.006	0.006	0.009	0.018	0.008
Sum	0.715	0.744	0.805	0.792	0.720	0.796	0.830	0.904	0.745	0.812	0.858	0.932	0.789	0.730	0.845	0.936
Furans																
2,3,7,8-TCDF	0.068	0.057	0.032	0.045	0.050	0.045	0.035	0.021	0.052	0.035	0.011 U	0.011	0.046	0.055	0.025	0.011
1,2,3,7,8-PECDF	0.010	0.008 J	0.006 J	0.007	0.009	0.007	0.006	0.003	0.008	0.006	0.005 J	0.002	0.008	0.009	0.004	0.002
2,3,4,7,8-PECDF	0.126	0.111 J	0.079 J	0.088	0.122	0.091	0.075	0.039	0.104	0.071	0.066 J	0.027	0.094	0.115	0.058	0.025
1,2,3,4,7,8-HXCDF	0.028 J	0.015 UJ	0.023 J	0.020	0.031	0.019	0.017	0.010	0.024	0.018	0.020 J	0.007	0.019	0.024	0.016	0.007
1,2,3,6,7,8-HXCDF	0.019 J	0.025 J	0.022 J	0.020	0.024	0.018	0.016	0.009	0.022	0.017	0.017 J	0.007	0.018	0.024	0.012	0.005
1,2,3,7,8,9-HXCDF	0.005 J	0.002 UJ	0.003 UJ	0.002 J	0.002 J	0.002 J	0.002 J	0.000 UJ	0.001 UJ	0.002 J	0.001 U	0.001 J	0.002 J	0.002 J	0.001 J	0.000 J
2,3,4,6,7,8-HXCDF	0.021 J	0.025 J	0.020 J	0.016	0.025	0.016	0.013	0.008	0.021	0.016	0.008 U	0.007	0.016	0.026	0.013	0.006
1,2,3,4,6,7,8-HPCDF	0.007	0.012	0.009	0.009	0.015	0.006	0.005	0.005	0.018	0.019	0.013 J	0.006	0.008	0.013	0.018	0.006
1,2,3,4,7,8,9-HPCDF	0.001 J	0.001 J	0.001 J	0.001	0.001	0.001	0.000	0.000	0.001	0.001	0.001 J	0.000	0.001	0.001	0.001	0.000
OCDF	0.000	0.000	0.000 J	0.000	0.001	0.000	0.000	0.000	0.004	0.002	0.001	0.000	0.001	0.001	0.005	0.001
Sum	0.285	0.256	0.195	0.208	0.280	0.204	0.170	0.096	0.255	0.188	0.142	0.068	0.211	0.270	0.155	0.064
Total 2,3,7,8-TCDD TEQ																
ND=0.5*DL	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Key:
DL = Sample-specific detection limit.
J = Concentration is estimated.
ND = Nondetect.
TEF = Toxicity equivalency factor.
TEQ = Total toxic equivalent concentration.
U = Analyte was not detected.

Table 6-4. Normalized TEQ contributions by congener.

	W204SS	W205SS	W206SS	W207SS	W208SS	W209SS	W210SS	W211SS	W212SS	W213SS	W214SS	W215SS	W216SS	W299SS	W301SS	W302SS
Congeners																
Dioxins																
2,3,7,8-TCDD	0.139	0.241	0.190	0.541	0.164	0.944	0.638	0.144	0.408	0.764	0.717	0.252	0.407	0.155	0.131	0.181
1,2,3,7,8-PECDD	0.409	0.259	0.310	0.204	0.365	0.022	0.172	0.376	0.208	0.104	0.097	0.340	0.164	0.392	0.416	0.319
1,2,3,4,7,8-HXCDD	0.040	0.030	0.037	0.021	0.037	0.002	0.017	0.038	0.022	0.008	0.010	0.036	0.016	0.036	0.034	0.033
1,2,3,6,7,8-HXCDD	0.068	0.084	0.088	0.040	0.073	0.005	0.030	0.081	0.068	0.022	0.027	0.065	0.062	0.065	0.061	0.058
1,2,3,7,8,9-HXCDD	0.074	0.077	0.084	0.041	0.074	0.005	0.032	0.090	0.058	0.018	0.019	0.067	0.051	0.069	0.069	0.076
1,2,3,4,6,7,8-HPCDD	0.041	0.084	0.090	0.028	0.068	0.005	0.019	0.081	0.085	0.020	0.045	0.050	0.118	0.032	0.036	0.043
OCDD	0.003	0.010	0.011	0.003	0.011	0.001	0.002	0.013	0.016	0.004	0.009	0.006	0.033	0.003	0.004	0.006
Sum	0.773	0.786	0.810	0.878	0.791	0.983	0.909	0.823	0.864	0.940	0.924	0.816	0.850	0.753	0.752	0.715
Furans																
2,3,7,8-TCDF	0.050	0.031	0.030	0.025	0.041	0.00232	0.018	0.031	0.021	0.013	0.008	0.041	0.027	0.058	0.052	0.072
1,2,3,7,8-PECDF	0.007	0.005	0.006	0.004	0.007	0.00038	0.003	0.006 J	0.004	0.002	0.002	0.006	0.004	0.010	0.009	0.007
2,3,4,7,8-PECDF	0.102	0.062	0.075	0.053	0.087	0.00633	0.040	0.075 J	0.049	0.026	0.019	0.081	0.058	0.119	0.115	0.129
1,2,3,4,7,8-HXCDF	0.021	0.022	0.021	0.011	0.020	0.00203	0.009	0.010 UJ	0.016	0.005	0.009	0.018	0.022	0.019	0.023	0.028
1,2,3,6,7,8-HXCDF	0.019	0.020	0.021	0.011	0.020	0.00190	0.008	0.018 J	0.013	0.005	0.007	0.016	0.010	0.019	0.020	0.018
1,2,3,7,8,9-HXCDF	0.002 J	0.002 J	0.001 J	0.001 J	0.002 J	0.00015 J	0.001 J	0.002 J	0.001 UJ	0.000 J	0.000 J	0.001 UJ	0.001 J	0.002 J	0.002 J	0.001 J
2,3,4,6,7,8-HXCDF	0.018	0.021	0.020	0.010	0.017	0.00222	0.008	0.018 J	0.012	0.005	0.006	0.013	0.010	0.016	0.020	0.017
1,2,3,4,6,7,8-HPCDF	0.007	0.049	0.015	0.005	0.014	0.00138	0.004	0.014	0.019	0.003	0.021	0.007	0.016	0.004	0.008	0.010
1,2,3,4,7,8,9-HPCDF	0.001	0.001	0.001	0.000	0.001	0.00009	0.000	0.001 J	0.001	0.000	0.001	0.001 J	0.001	0.000	0.001	0.001
OCDF	0.000	0.001	0.001	0.0002	0.001	0.00007	0.000	0.001	0.001	0.000	0.002	0.000	0.001	0.000	0.000	0.001
Sum	0.227	0.214	0.190	0.122	0.209	0.017	0.091	0.177	0.136	0.060	0.076	0.184	0.150	0.247	0.248	0.285
Total 2,3,7,8-TCDD TEQ																
ND=0.5*DL	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Key:

DL = Sample-specific detection limit.

J = Concentration is estimated.

ND = Nondetect.

TEF = Toxicity equivalency factor.

TEQ = Total toxic equivalent concentration.

U = Analyte was not detected.

Table 6-4. Normalized TEQ contributions by congener.

	W303SS	W304SS	W305SS	W306SS
Congeners				
Dioxins				
2,3,7,8-TCDD	0.159	0.548	0.214	0.391
1,2,3,7,8-PECDD	0.389	0.172	0.311	0.241
1,2,3,4,7,8-HXCDD	0.035	0.018	0.030	0.026
1,2,3,6,7,8-HXCDD	0.066	0.044	0.065	0.048
1,2,3,7,8,9-HXCDD	0.072	0.038	0.060	0.052
1,2,3,4,6,7,8-HPCDD	0.043	0.064	0.091	0.046
OCDD	0.005	0.013	0.021	0.008
Sum	0.769	0.898	0.792	0.813
Furans				
2,3,7,8-TCDF	0.050	0.018	0.035	0.033
1,2,3,7,8-PECDF	0.009	0.003	0.006	0.006
2,3,4,7,8-PECDF	0.102	0.043	0.086	0.080
1,2,3,4,7,8-HXCDF	0.019	0.011	0.021	0.018
1,2,3,6,7,8-HXCDF	0.020	0.009	0.016	0.018
1,2,3,7,8,9-HXCDF	0.002 J	0.001 J	0.002 J	0.002 J
2,3,4,6,7,8-HXCDF	0.019	0.009	0.018	0.018
1,2,3,4,6,7,8-HPCDF	0.009	0.007	0.021	0.011
1,2,3,4,7,8,9-HPCDF	0.001	0.001	0.001	0.001
OCDF	0.000	0.001	0.002	0.001
Sum	0.231	0.102	0.208	0.187
Total 2,3,7,8-TCDD TEQ				
ND=0.5*DL	1.0	1.0	1.0	1.0

Key:
DL = Sample-specific detection limit.
J = Concentration is estimated.
ND = Nondetect.
TEF = Toxicity equivalency factor.
TEQ = Total toxic equivalent concentration.
U = Analyte was not detected.

Table 8-1 Comparison soils datasets: summary statistics

Location	Reference	Number of Samples	Range (ng/kg TEQ)	Median (ng/kg TEQ)	75th Percentile (ng/kg TEQ)
Port Angeles, WA	this study				
grid		60	1.13 - 76.26	11.87	17.45
forest		14	4.02 - 40.46	10.61	25.58
upslope		9	0.80 - 5.54	1.82	2.37
road		2	4.04 - 6.50	5.27	6.50
Bellingham, WA	Ecology & Environment 2002				
[Oeser Site background]					
residential (ND=1/2DL)		10	1.48 - 34.76	7.32	11.29
residential (ND=0)		10	0.83 - 22.93	4.78	7.42
open (ND=1/2DL)		10	0.70 - 4.11	2.22	2.75
open (ND=0)		10	0.17 - 2.96	1.16	1.72
Washington State Survey	Rogowski et al. 1999				
urban	Rogowski and Yake 2005	14	0.73 - 21.55	2.74	5.92
forest		8	1.18 - 6.67	3.49	5.60
open		8	0.69 - 5.18	1.47	2.31
Denver, Colorado	USEPA, Region 8, 2001	38	0.21 - 42.71	2.17	7.92
Davis County, Utah	University of Utah (undated)	22	0.32 - 4.47	0.90	1.83
Australia National Survey	Muller et al. 2004				
urban		27	0.11 - 45.33	4.18	10.74
Trondheim, Norway	Andersson and Ottesen 2007	49	0.16 - 12.13	1.51	2.30
	Andersson 2009				
US Survey	USEPA 2007				
rural soils		27	0.21 - 11.69	0.94	2.32
Michigan	Demond et al. 2008				

Table 8-1 Comparison soils datasets: summary statistics

Location	Reference	Number of Samples	Range (ng/kg TEQ)	Median (ng/kg TEQ)	75th Percentile (ng/kg TEQ)
Jackson/Calhoun Counties					
house perimeter 0–1 inches		194	3–64.1	2.9	5.7
house perimeter 1–6 inches		53	7–31.9	6.8	8.7
garden		124	2–18.5	2.0	4.0
Switzerland					
forest	Schmid et al.	11	2.33–11.95	4.58	6.59

Note: All results are summarized based on 2005 WHO TEFs (Van den Berg et al. 2006), except for Utah results, which are as reported by the authors. Detailed congener results for the Utah samples were unavailable, precluding recalculation of TEQs. The individual sample results for Michigan are not reported, but the authors (Demond et al. 2008) report TEQs based on 2005 WHO TEFs. The statistical parameters for TEQ results for Michigan are as reported by the authors.

Table 8-2 Unmixing model: fractional source contributions to samples

Sample ID	Sample Index No.	Source 1	Source 2	Source 3
E102SS	1	0.2374	0.1650	0.5976
E103SS	2	0.3273	0.2693	0.4034
E105SS	3	0.0022	0.3223	0.6755
E106SS	4	0.0649	0.3217	0.6134
E108SS	5	0.0268	0.4990	0.4743
E109SS	6	0.0157	0.2448	0.7395
E110SS	7	0.0181	0.5060	0.4759
E111SS	8	0.0156	0.2465	0.7379
E116SS	9	0.0000	0.2224	0.7776
E117SS	10	0.0000	0.2970	0.7030
E121SS	11	0.0361	0.3788	0.5851
E122SS	12	0.4106	0.2027	0.3867
E194SS	13	0.0192	0.1944	0.7863
E195SS	14	0.0196	0.5473	0.4331
E196SS	15	0.0322	0.3479	0.6199
E197SS	16	0.4199	0.1517	0.4284
E198SS	17	0.0000	0.2787	0.7213
E199SS	18	0.0958	0.3194	0.5848
E201SS	19	0.0000	0.2425	0.7575
E204SS	20	0.0939	0.4230	0.4832
E206SS	21	0.0066	0.2021	0.7914
E208SS	22	0.0000	0.2402	0.7598
E298SS	23	0.0314	0.3866	0.5820
E299SS	24	0.0329	0.9671	0.0000
E302SS	25	0.0287	0.2142	0.7571
E402SS	26	0.0128	0.2416	0.7455
T101SS	43	0.0278	0.4900	0.4821
T103SS	44	0.0033	0.1841	0.8126
T104SS	45	0.0463	0.8518	0.1020
T201SS	46	0.0053	0.2087	0.7860
T202SS	47	0.0345	0.3949	0.5706
T203SS	48	0.0289	0.2607	0.7104
T301SS	49	0.0070	0.1976	0.7953
T302SS	50	0.0432	0.3342	0.6226
T303SS	51	0.0015	0.7692	0.2293
W102SS	52	0.1276	0.2884	0.5840
W103SS	53	0.0272	0.2838	0.6890
W104SS	54	0.1013	0.2243	0.6744
W105SS	55	0.1348	0.2098	0.6554
W107SS	56	0.5926	0.1461	0.2613
W108SS	57	0.0236	0.3121	0.6643
W109SS	58	0.0379	0.5160	0.4462
E112SS	59	0.0000	0.3578	0.6422
W196SS	60	0.0105	0.5856	0.4039
W197SS	61	0.6868	0.1246	0.1886
W198SS	62	0.0538	0.2440	0.7022
W201SS	63	0.0443	0.2769	0.6788
W202SS	64	0.4580	0.2729	0.2691
W203SS	65	0.8110	0.1366	0.0524
W204SS	66	0.0283	0.2012	0.7705
W205SS	67	0.2285	0.5327	0.2388
W206SS	68	0.1403	0.5069	0.3528

Table 8-2 Unmixing model: fractional source contributions to samples

Sample ID	Sample Index No.	Source 1	Source 2	Source 3
E403SS	27	0.0724	0.5079	0.4197
E405SS	28	0.3459	0.1992	0.4550
E406SS	29	0.0000	0.1010	0.8990
E498SS	30	0.0364	0.2882	0.6754
E499SS	31	0.9623	0.0295	0.0083
FF01SS	32	0.0279	0.3002	0.6719
FF02SS	33	0.0233	0.0870	0.8897
FF03SS	34	0.0400	0.1306	0.8294
FF04SS	35	0.0248	0.0677	0.9075
FF05SS	36	0.0061	0.2030	0.7910
FF06SS	37	0.0246	0.1269	0.8485
FF07SS	38	0.0196	0.1027	0.8777
FF08SS	39	0.0218	0.1194	0.8588
FF09SS	40	0.0165	0.0896	0.8939
RD01SS	41	0.0546	0.9454	0.0000
RD02SS	42	0.4093	0.4382	0.1525
W207SS	69	0.5605	0.1170	0.3226
W208SS	70	0.0821	0.3499	0.5680
W209SS	71	1.0000	0.0000	0.0000
W210SS	72	0.6749	0.0625	0.2626
W211SS	73	0.0618	0.4380	0.5002
W212SS	74	0.4301	0.4480	0.1220
W213SS	75	0.8508	0.0473	0.1020
W214SS	76	0.8122	0.1878	0.0000
W215SS	77	0.1833	0.2485	0.5682
W216SS	78	0.4461	0.5539	0.0000
W299SS	79	0.0476	0.1400	0.8124
W301SS	80	0.0144	0.1562	0.8294
W302SS	81	0.1081	0.1839	0.7080
W303SS	82	0.0585	0.2108	0.7307
W304SS	83	0.5898	0.2837	0.1265
W305SS	84	0.1666	0.4338	0.3996
W306SS	85	0.3914	0.2099	0.3987

Note: The sample index numbers reflect an ordering of samples by sample zone/sample type, except that sample E112SS was mislabeled in the field as W112SS and is listed for sample index codes with the Zone W1 samples. All data evaluations correctly placed sample E112SS in Zone E1. Sample index numbers are used in Figure 8-11 to summarize unmixing model sample compositions (fractional source contributions).

Table 8-3 Unmixing model: source increment TEQs

Sample ID	Sample Index No.	Source 1	Source 2	Source 3	Total TEQ
E102SS	1	3.6042	2.5053	9.0741	15.2
E103SS	2	5.3915	4.4363	6.6453	16.5
E105SS	3	0.0320	4.6064	9.6549	14.3
E106SS	4	1.1509	5.7063	10.8790	17.7
E108SS	5	0.3685	6.8661	6.5262	13.8
E109SS	6	0.4119	6.4240	19.4088	26.2
E110SS	7	0.0751	2.0975	1.9730	4.15
E111SS	8	0.1996	3.1456	9.4184	12.8
E116SS	9	0.0000	1.4005	4.8974	6.30
E117SS	10	0.0000	3.2516	7.6974	10.9
E121SS	11	0.1226	1.2863	1.9870	3.4
E122SS	12	4.2921	2.1183	4.0424	10.5
E194SS	13	0.1143	1.1545	4.6696	5.94
E195SS	14	0.1846	5.1672	4.0889	9.44
E196SS	15	0.0818	0.8830	1.5732	2.54
E197SS	16	11.1793	4.0374	11.4046	26.6
E198SS	17	0.0000	3.9867	10.3196	14.3
E199SS	18	0.6323	2.1083	3.8595	6.60
E201SS	19	0.0000	3.6617	11.4354	15.1
E204SS	20	0.4743	2.1379	2.4420	5.05
E206SS	21	0.0602	1.8549	7.2636	9.18
E208SS	22	0.0000	0.9228	2.9187	3.84
E298SS	23	0.2468	3.0419	4.5795	7.87
E299SS	24	0.2727	8.0213	0.0000	8.29
E302SS	25	0.1186	0.8866	3.1334	4.14
E402SS	26	0.0521	0.9819	3.0294	4.06
E403SS	27	2.9274	20.5493	16.9812	40.5
T101SS	43	0.0506	0.8903	0.8760	1.82
T103SS	44	0.0072	0.4036	1.7814	2.19
T104SS	45	0.1107	2.0382	0.2440	2.39
T201SS	46	0.0293	1.1565	4.3565	5.54
T202SS	47	0.0446	0.5113	0.7388	1.29
T203SS	48	0.0684	0.6177	1.6831	2.37
T301SS	49	0.0117	0.3300	1.3281	1.67
T302SS	50	0.0347	0.2683	0.4999	0.80
T303SS	51	0.0018	0.9223	0.2749	1.20
W102SS	52	1.3623	3.0797	6.2365	10.7
W103SS	53	0.2289	2.3871	5.7962	8.41
W104SS	54	1.5432	3.4191	10.2779	15.2
W105SS	55	2.3064	3.5886	11.2132	17.1
W107SS	56	15.5599	3.8362	6.8612	26.3
W108SS	57	0.2028	2.6851	5.7148	8.60
W109SS	58	0.3657	4.9833	4.3091	9.66
E112SS	59	0.0000	6.5000	11.6684	18.2
W196SS	60	0.0119	0.6605	0.4555	1.13
W197SS	61	15.2027	2.7577	4.1755	22.1
W198SS	62	1.1864	5.3820	15.4912	22.1
W201SS	63	0.5047	3.1576	7.7398	11.4
W202SS	64	5.9169	3.5247	3.4763	12.9
W203SS	65	18.8034	3.1665	1.2153	23.2
W204SS	66	0.4931	3.5114	13.4474	17.5
W205SS	67	2.3311	5.4355	2.4367	10.2
W206SS	68	1.9399	7.0076	4.8781	13.8
W207SS	69	7.6877	1.6042	4.4244	13.7

Table 8-3 Unmixing model: source increment TEQs

Sample ID	Sample Index No.	Source 1	Source 2	Source 3	Total TEQ
E405SS	28	2.6407	1.5207	3.4735	7.63
E406SS	29	0.0000	0.6517	5.8002	6.45
E498SS	30	0.2799	2.2155	5.1919	7.69
E499SS	31	19.1476	0.5860	0.1643	19.9
FF01SS	32	0.7569	8.1431	18.2293	27.1
FF02SS	33	0.2118	0.7917	8.0925	9.10
FF03SS	34	0.3159	1.0301	6.5417	7.89
FF04SS	35	0.4562	1.2468	16.7047	18.4
FF05SS	36	0.0243	0.8155	3.1780	4.02
FF06SS	37	0.6301	3.2460	21.7068	25.6
FF07SS	38	0.2935	1.5364	13.1309	15.0
FF08SS	39	0.1394	0.7652	5.5027	6.41
FF09SS	40	0.5650	3.0606	30.5416	34.2
RD01SS	41	0.3547	6.1421	0.0000	6.50
RD02SS	42	1.6551	1.7721	0.6167	4.04
W208SS	70	0.4815	2.0523	3.3312	5.87
W209SS	71	76.2616	0.0000	0.0000	76.3
W210SS	72	17.2541	1.5974	6.7125	25.6
W211SS	73	0.1088	0.7705	0.8799	1.76
W212SS	74	2.5484	2.6544	0.7227	5.93
W213SS	75	24.4848	1.3602	2.9352	28.8
W214SS	76	22.4147	5.1833	0.0000	27.6
W215SS	77	1.2681	1.7191	3.9303	6.92
W216SS	78	7.7865	9.6670	0.0000	17.5
W299SS	79	0.5731	1.6852	9.7771	12.0
W301SS	80	0.1684	1.8320	9.7267	11.7
W302SS	81	1.4231	2.4211	9.3201	13.2
W303SS	82	0.6556	2.3637	8.1917	11.2
W304SS	83	13.9980	6.7334	3.0029	23.7
W305SS	84	0.7618	1.9836	1.8269	4.57
W306SS	85	4.6987	2.5193	4.7866	12.0

Note: The sample index numbers reflect an ordering of samples by sample zone/sample type, except that sample E112SS was mislabeled in the field as W112SS and is listed for sample index codes with the Zone W1 samples. All data evaluations correctly placed sample E112SS in Zone E1. The modeled contributions of each source to each sample (source increment TEQs) are used in detailed evaluations of the magnitudes and spatial patterns associated with individual modeled sources, as well as estimates of the mass emissions associated with Source 3 (see Sections 8.3 and 8.4).

Figures

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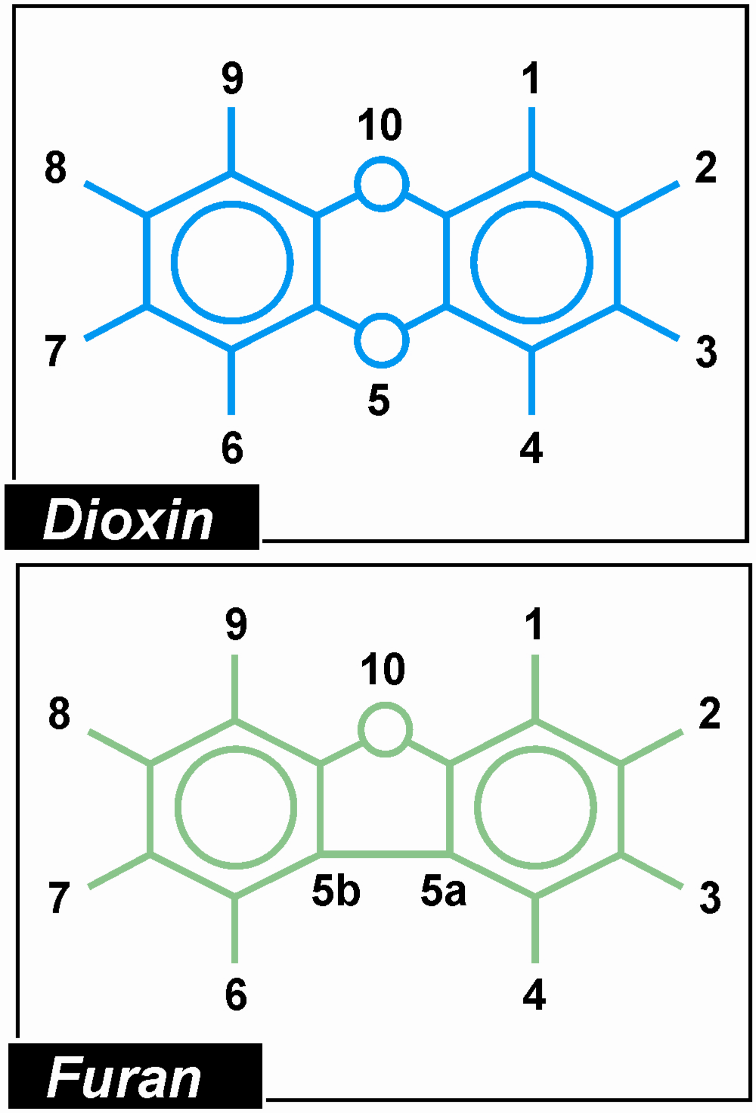

Figure 1-1 Structure and chlorine substitution locations for dioxins and furans

Figure 2-1.
Potential Fixed Sources of Dioxins/Furans in Port Angeles Rayonier Mill Off-Property Soil Dioxin Study Port Angeles, WA

Legend

Potential Dioxins/Furans Sources

- ● Current Boiler
- ● Current Crematoria
- ● Current Diesel Boiler
- ● Current Hog Boiler
- ● Current Propane Boiler
- ● Historic Sawmill
- ● Historic Hog Boiler
- ● Historic medical waste incinerator
- River
- Highway
- Arterial or Collector Road
- Road
- ☐ Study Area Boundary
- ☐ Port Angeles City Limits

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HERRERA ENVIRONMENTAL CONSULTANTS

0 1,250 2,500 5,000 feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (JAS)
Project:
K:/Projects/06-03386-006/Projects/Dioxin and Furan Sources.mxd (06/22/2011)

Figure 3-1
Study Area Boundary
Rayonier Mill Off-Property
Soil Dioxin Study
Port Angeles, WA

Legend

- 🟨 Study Area Boundary
- River
- Highway
- Arterial or Collector Road
- Road
- 🟧 Port Angeles City Limits
- 🟩 Park

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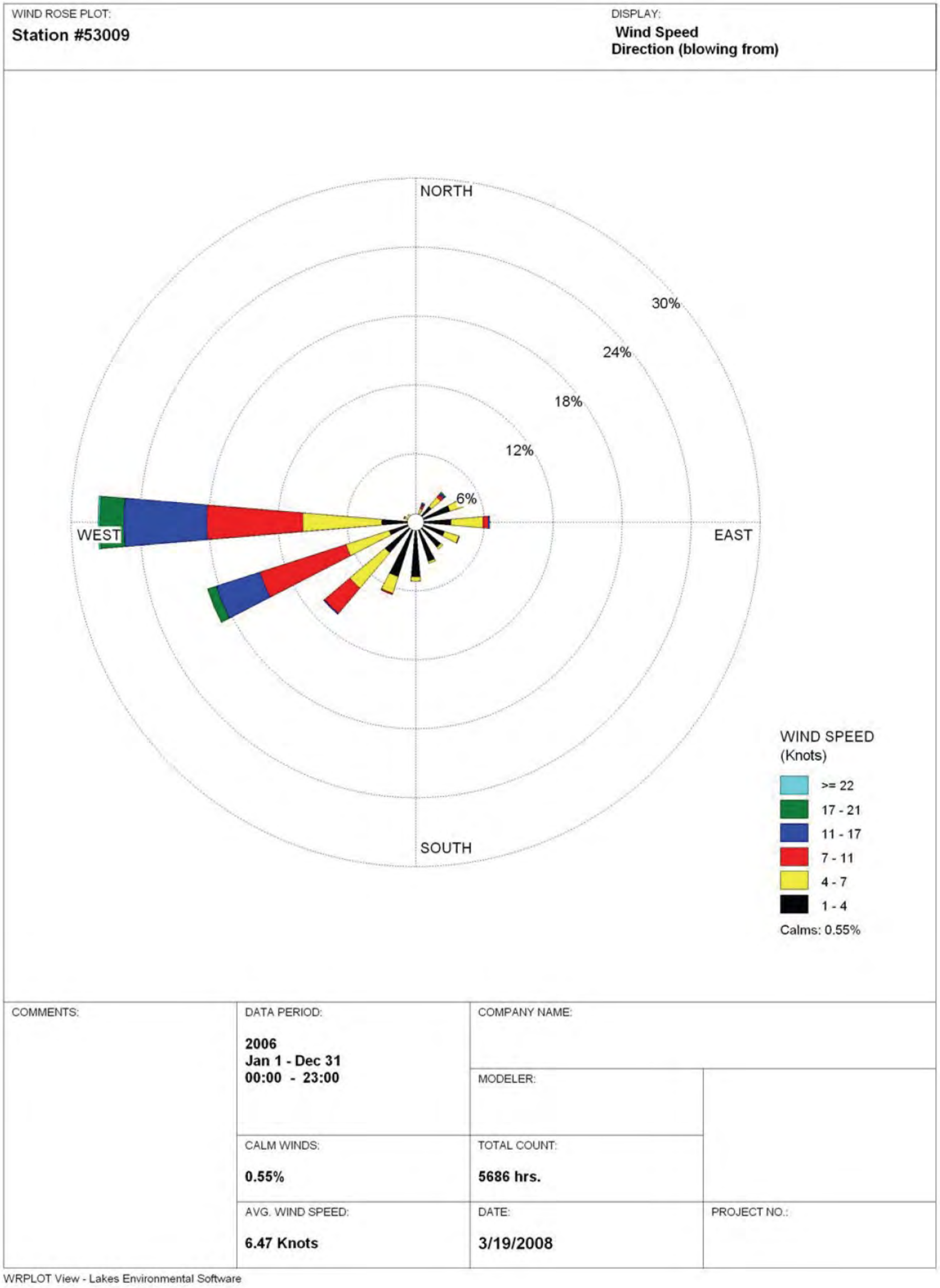
0 1,250 2,500 5,000 feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

Produced By: GIS (JAS)
Project:
K:/Projects/06-03386-006/Projects/Study Area Grid Overview.mxd (06/06/2008)



WIND ROSE PLOT:

Station #53009

DISPLAY:

Wind Speed
Direction (blowing from)

COMMENTS:

DATA PERIOD:

2006
Jan 1 - Dec 31
00:00 - 23:00

COMPANY NAME:

MODELER:

CALM WINDS:

0.55%

TOTAL COUNT:

5686 hrs.

AVG. WIND SPEED:

6.47 Knots

DATE:

3/19/2008

PROJECT NO.:

WRPLOT View - Lakes Environmental Software

Figure 3-2 Wind rose for Ediz Hook, Port Angeles – 2006

Figure 3-3
Sample Zones
Rayonier Mill Off-Property
Soil Dioxin Study
Port Angeles, WA

Legend

▭	Sample Zone Boundary
‒·‒	River
―	Highway
―	Arterial or Collector Road
―	Road
▭	Port Angeles City Limits
🟩	Park

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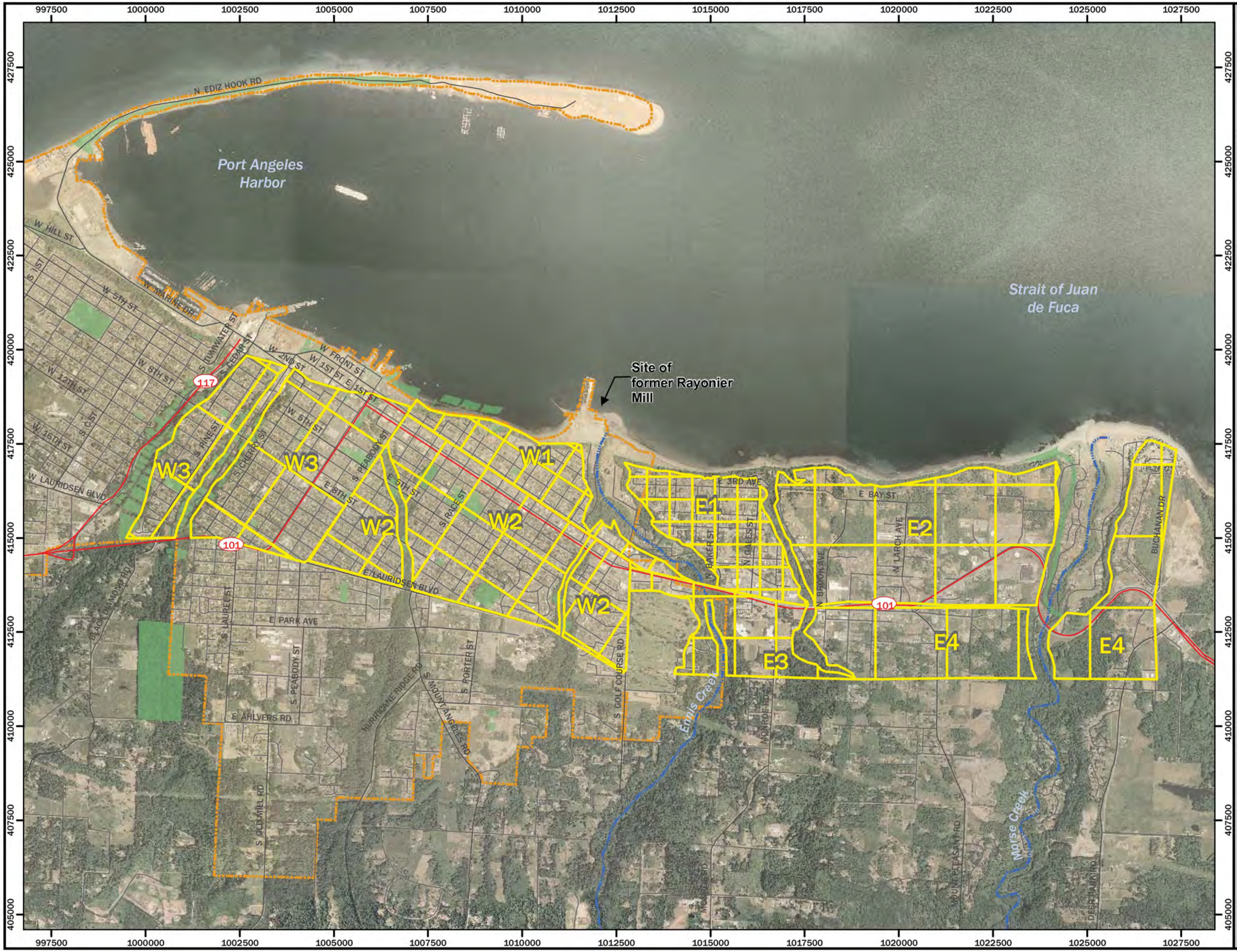
0 1,250 2,500 5,000
feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (JAS)
Project:
K:/Projects/06-03386-006/Projects/Study Area Zones.mxd (06/06/2008)

Figure 3-4
Sample Grid Spacing
Rayonier Mill Off-Property
Soil Dioxin Study
Port Angeles, WA



Legend

▭ Grid Cell Boundary

River

Highway

Arterial or Collector Road

Road

Port Angeles City Limits

🟩 Park

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0 1,250 2,500 5,000 feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (JAS)
Project:
K:/Projects/06-03386-006/Projects/Study Area Grids.mxd (09/09/2008)

Figure 3-5
Generalized Upslope Transect Sampling Areas
Rayonier Mill Off-Property Soil Dioxin Study
Port Angeles, WA

Legend

- ▨ Upslope Transect Sampling Area
- ☐ Study Area Boundary
- River
- Highway
- Arterial or Collector Road
- Road

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0 2,250 4,500 9,000 feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (JAS)
Project:
K:/Projects/06-03386-006/Projects/Transect Locations.mxd (06/06/2008)

Figure 4-1
Samples collected in zone W1.
Rayonier Mill Off-Property
Soil Dioxin Study
Port Angeles, WA.

Legend

Soil sample type

▲ Forested

● Grid

🟥 Highway

◆ Transect

☐ Grid cell boundary

— Arterial or Collector Road

— Road

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0 325 650 1,300
feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (RDR)
Project:
K:/Projects/06-03386-006/Collected_Samples/Samples Collected in Zone W-1.mxd (02/19/2009)

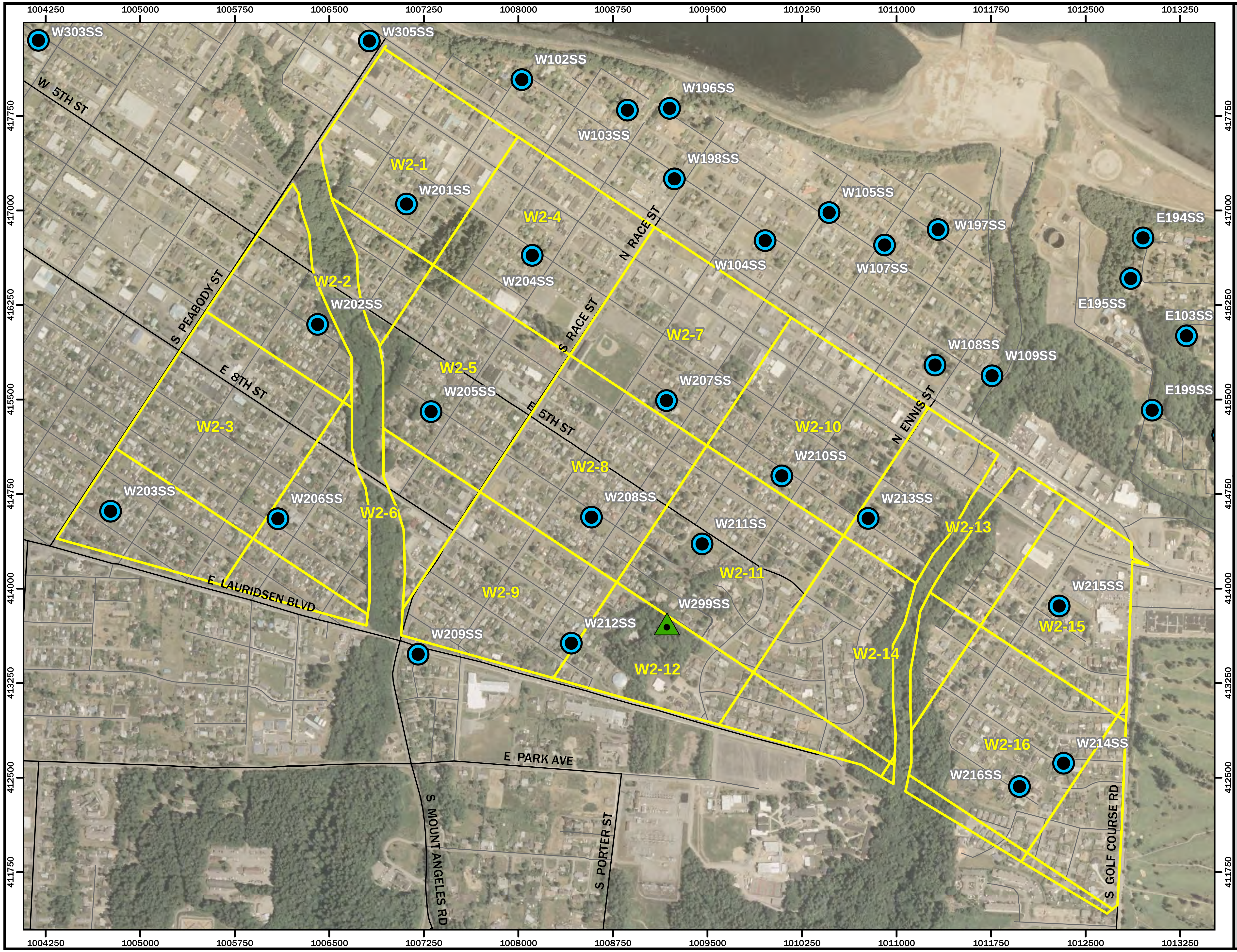

Figure 4-2
Samples collected in zone W2.
Rayonier Mill Off-Property
Soil Dioxin Study
Port Angeles, WA.

Legend

Soil sample type

▲ Forested

● Grid

🟥 Highway

◆ Transect

▭ Grid cell boundary

— Arterial or Collector Road

— Road

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0 375 750 1,500
feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (JAS)
Project:
K:/Projects/06-03386-006/Collected_Samples/Samples Collected in Zone W-2.mxd (11/23/2009)

Figure 4-3.
Samples collected in zone W3
Rayonier Mill Off-Property
Soil Dioxin Study
Port Angeles, WA.

Legend

Soil sample type

- ▲ Forested
- ● Grid
- 🟥 Highway
- ◆ Transect
- ☐ Grid cell boundary
- ― Arterial or Collector Road
- ― Road

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HERRERA
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0 325 650 1,300
feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (RDR)
Project:
K:/Projects/06-03386-006/Collected_Samples/Samples Collected in Zone W-3.mxd (02/19/2009)

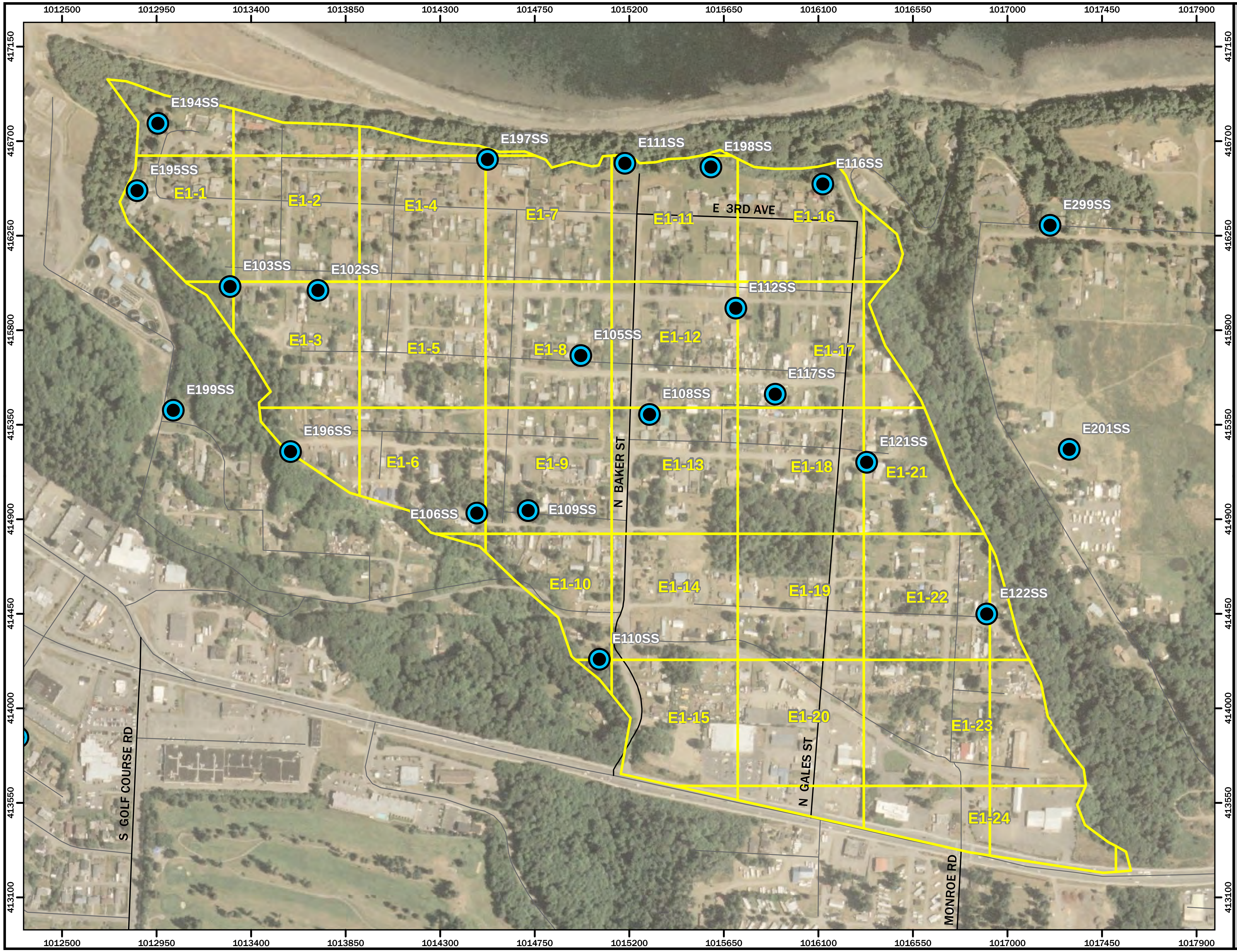

Figure 4-4.
Samples collected in zone E1
Rayonier Mill Off-Property
Soil Dioxin Study
Port Angeles, WA

Legend

Soil sample type

- ▲ Forested
- ● Grid
- 🟥 Highway
- ◆ Transect
- ▭ Grid cell boundary
- — Arterial or Collector Road
- — Road

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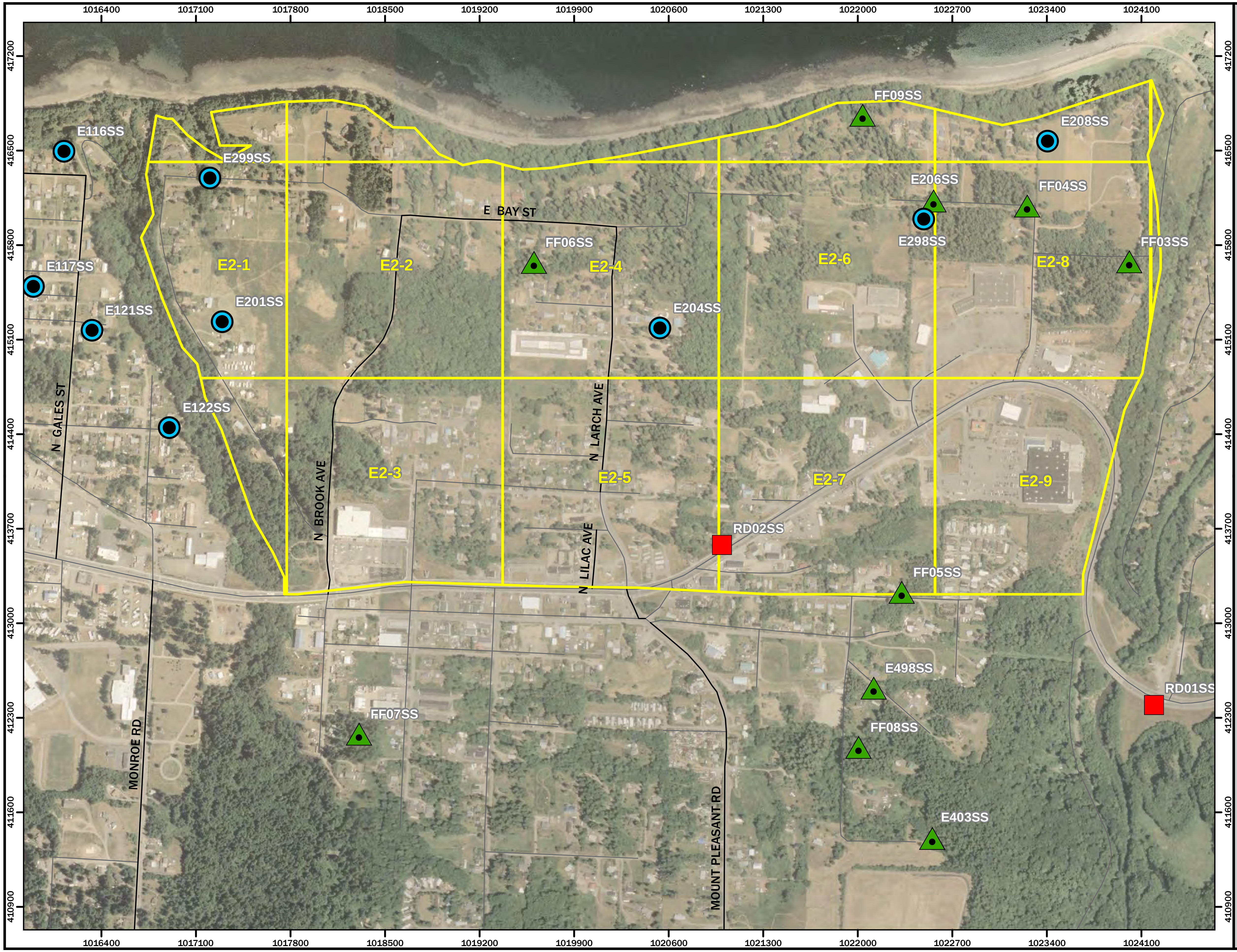
0 225 450 900 feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (RDR)
Project:
K:/Projects/06-03386-006/Collected_Samples/Samples Collected in Zone E-1.mxd (02/19/2009)

Figure 4-5.
Samples collected in zone E2.
Rayonier Mill Off-Property
Soil Dioxin Study
Port Angeles, WA



Legend

Soil sample type

- ▲ Forested
- ● Grid
- 🟥 Highway
- ◆ Transect
- Arterial or Collector Road
- Road

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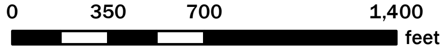
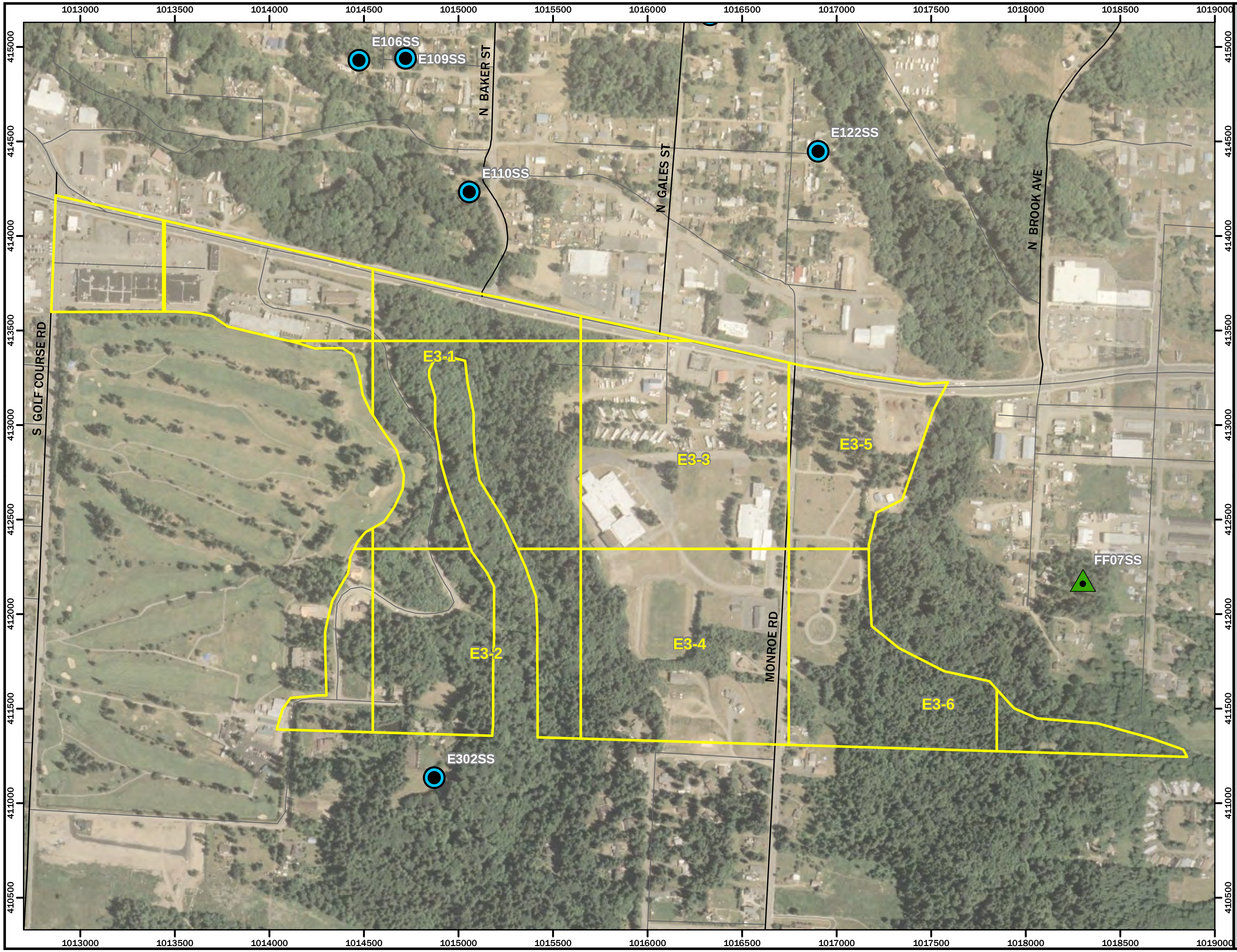
HERRERA
ENVIRONMENTAL CONSULTANTS



Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

Produced By: GIS (JAS)
Project:
K:/Projects/06-03386-006/Collected_Samples/Samples Collected in Zone E-2.mxd (11/23/2009)

Figure 4-6.
Samples collected in zone E3
Rayonier Mill Off-Property
Soil Dioxin Study
Port Angeles, WA



Legend

Soil sample type

- ▲ Forested
- ◉ Grid
- 🟥 Highway
- ◆ Transect
- ▭ Grid cell boundary
- — Arterial or Collector Road
- — Road

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0 250 500 1,000 feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (RDR)
Project:
K:/Projects/06-03386-006/Collected_Samples/Samples Collected in Zone E-3.mxd (02/19/2009)

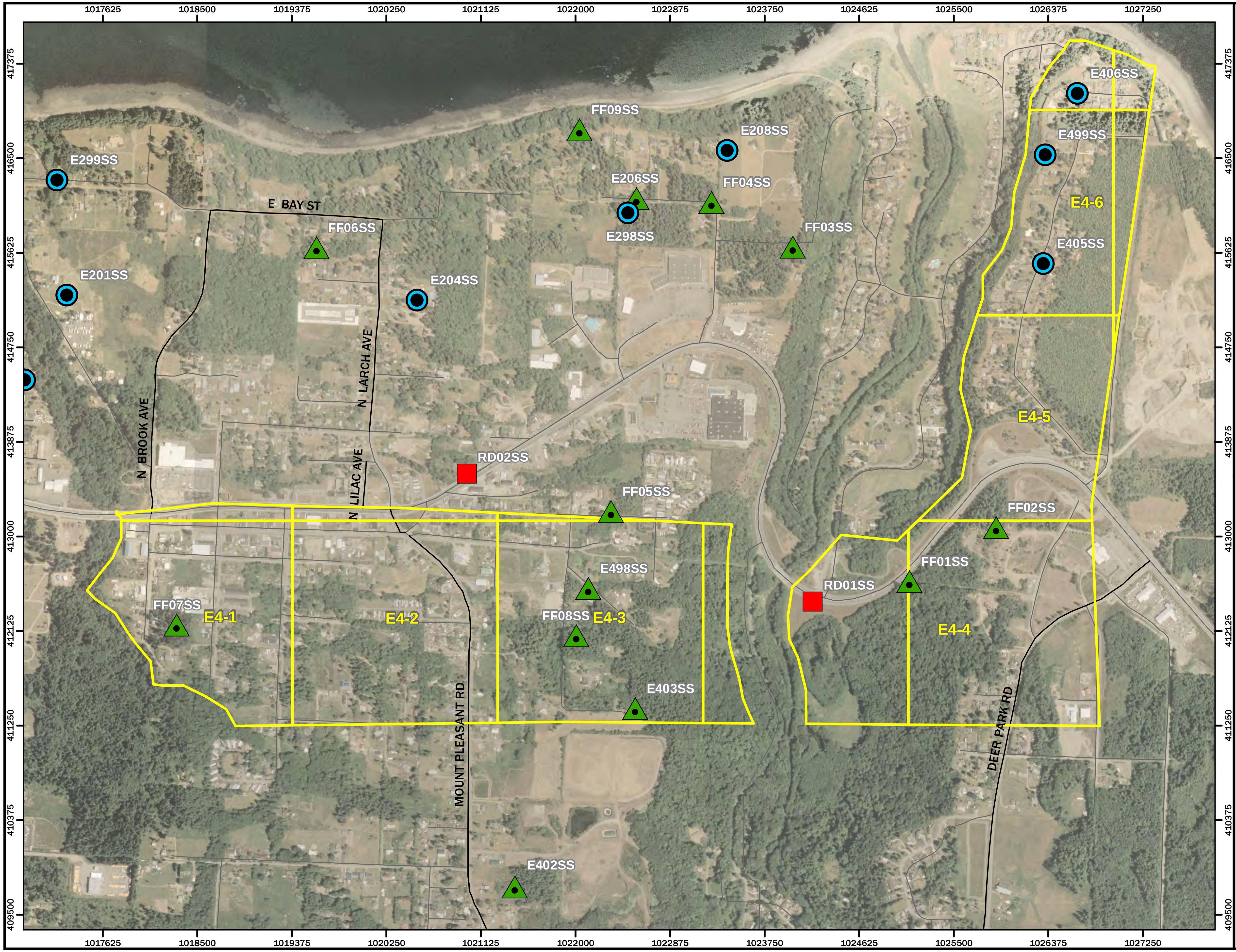

Figure 4-7
Samples collected in zone E4
Rayonier Mill Off-Property
Soil Dioxin Study
Port Angeles, WA

Legend

Soil sample type

- ▲ Forested
- ● Grid
- 🟥 Highway
- ◆ Transect
- ☐ Grid cell boundary
- — Arterial or Collector Road
- — Road

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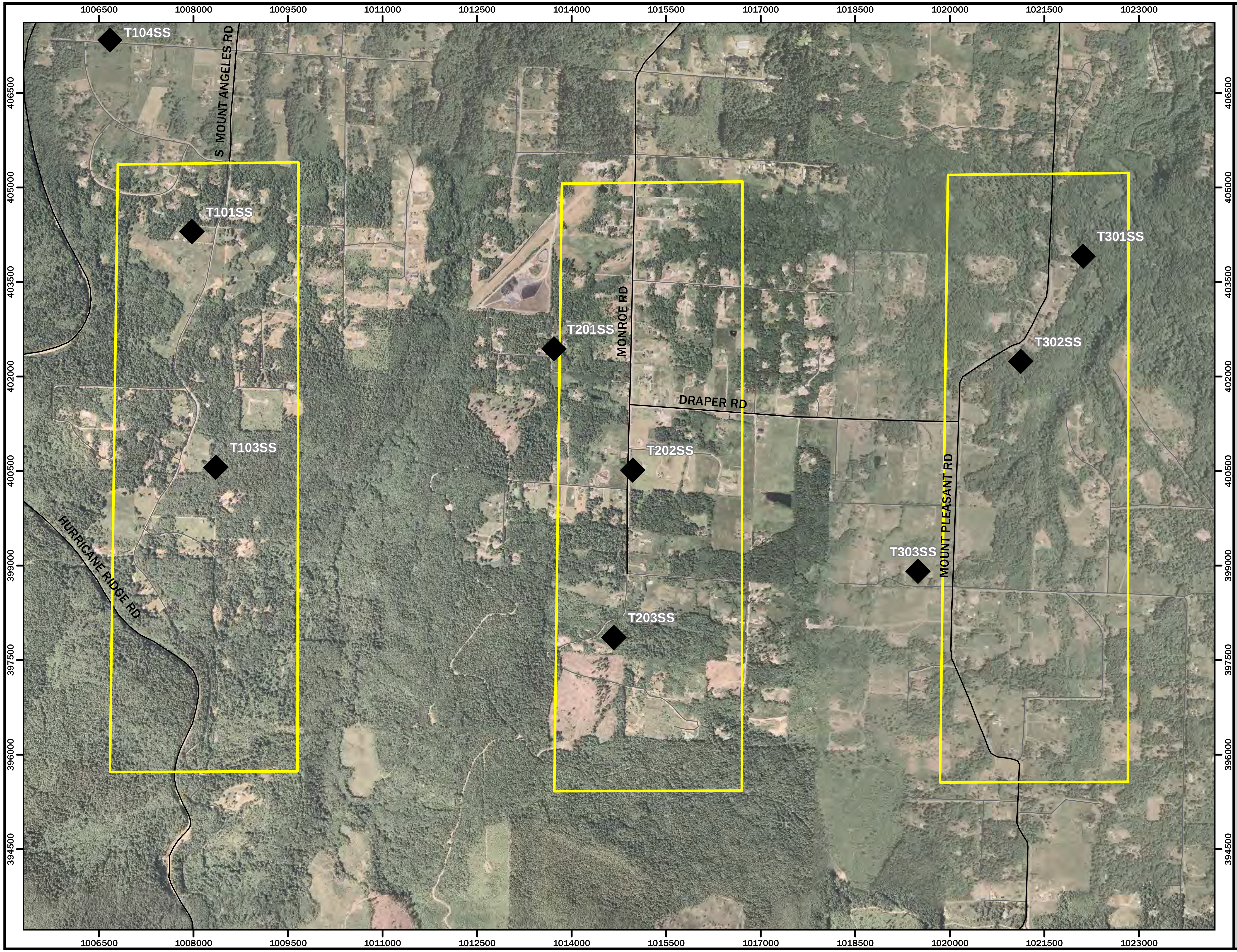
0 437.5 875 1,750 feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (RDR)
Project:
K:/Projects/06-03386-006/Collected_Samples/Samples Collected in Zone E-4.mxd (02/19/2009)

Figure 4-8.
Samples collected in upslope transect areas
Rayonier Mill Off-Property Soil Dioxin Study
Port Angeles, WA



Legend

Soil sample type

▲ Forested

◎ Grid

🟥 Highway

◆ Transect

▭ Upslope transect boundary

—— Arterial or Collector Road

—— Road

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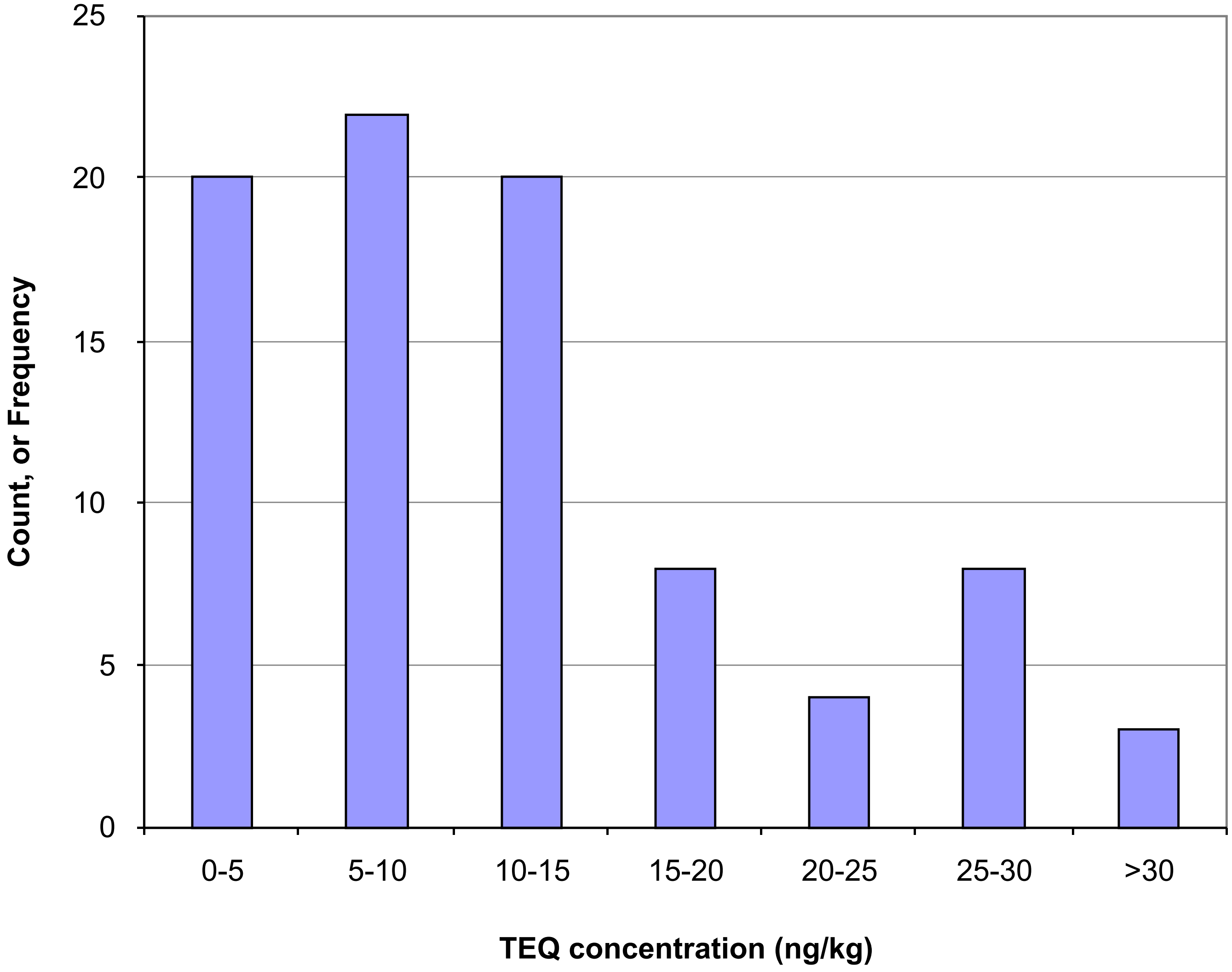
0 750 1,500 3,000
feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (RDR)
Project:
K:/Projects/06-03386-006/Collected_Samples/Samples Collected in Upslope Transects.mxd (02/19/2009)



Notes: Total sample count is 85.
TEQs based on ND=1/2DL.

Figure 6-1 Histogram of TEQ concentrations

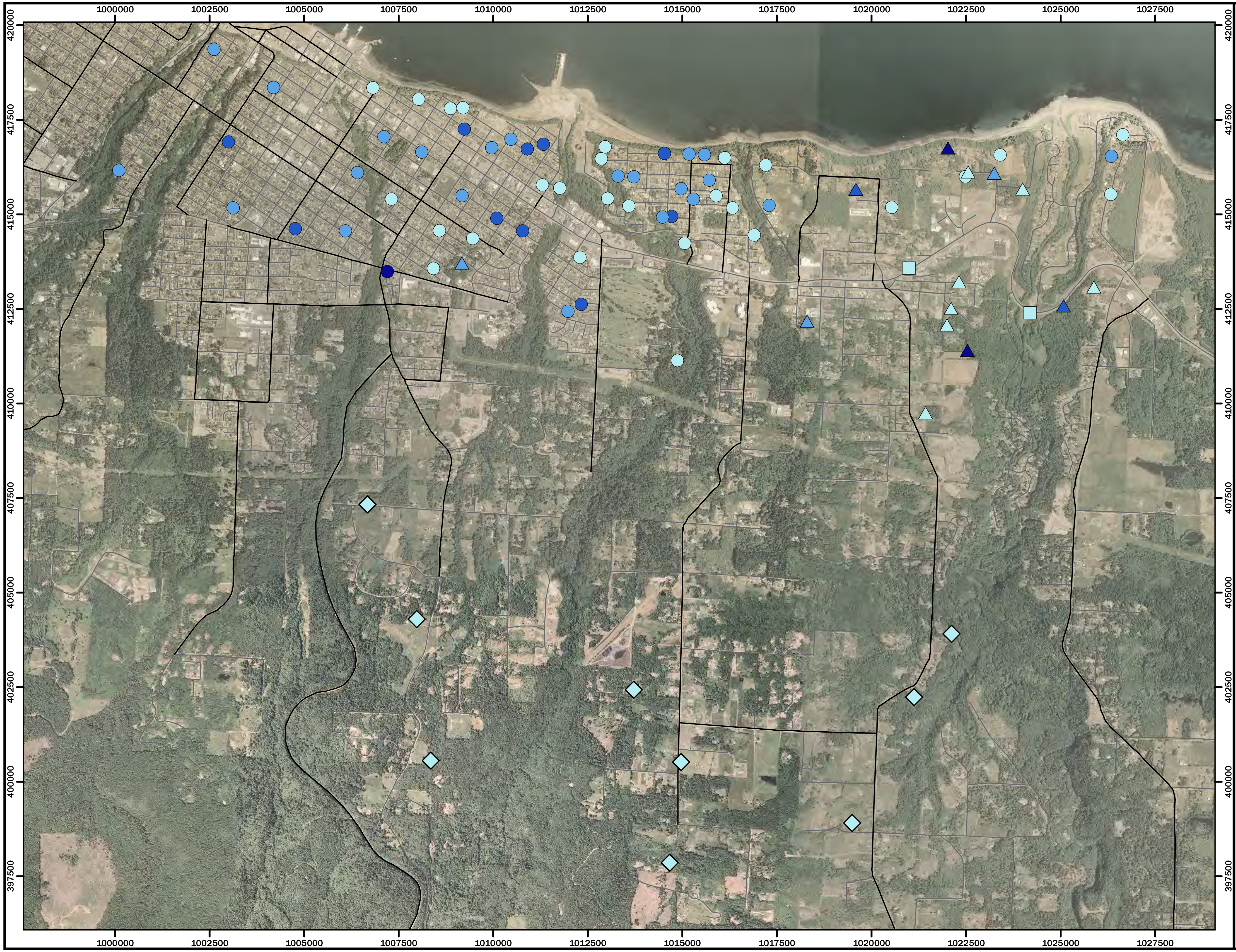


Figure 6-2.
Overview of TEQ concentrations across study area
Rayonier Mill Off-Property
Soil Dioxin Study
Port Angeles, WA

Legend

TEQ (ND=1/2 DL) concentrations shown in ng/kg
TEQ (ND=1/2 DL) range = 0.8 to 76.3 ng/kg

- ● 0 to 11
- ● 11 to 20
- ● 20 to 30
- ● > 30

Soil sample type

- △ Forested
- ○ Grid
- □ Highway
- ◇ Transect
- — Arterial or Collector Road
- — Road

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0 1,250 2,500 5,000
feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (RDR)
Project:
K:/Projects/06-03386-006/Collected_Samples/TEQ_Calc/TEQ Sample Overview.mxd (02/19/2009)

Figure 6-3.

TEQ concentrations in Western zones
Rayonier Mill Off-Property
Soil Dioxin Study
Port Angeles, WA.

Legend

TEQ (ND=1/2 DL) concentrations shown in ng/kg

- ● 0 to 11
- ● 11 to 20
- ● 20 to 30
- ● > 30

Soil sample type

- △ Forested
- ○ Grid
- □ Highway
- ◇ Transect
- ▭ Grid cell boundary
- — Arterial or Collector Road
- — Road

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0 600 1,200 2,400
feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (RDR)
Project:
K:/Projects/06-03386-006/Collected_Samples/Samples Collected in Western Zone.mxd (02/19/2009)

Figure 6-4.
TEQ concentrations in Eastern zones
Rayonier Mill Off-Property
Soil Dioxin Study
Port Angeles, WA

Legend

TEQ (ND=1/2 DL) concentrations shown in ng/kg

- ● 0 to 11
- ● 11 to 20
- ● 20 to 30
- ● > 30

Soil sample type

- △ Forested
- ○ Grid
- □ Highway
- ◇ Transect
- ▭ Grid cell boundary
- — Arterial or Collector Road
- — Road

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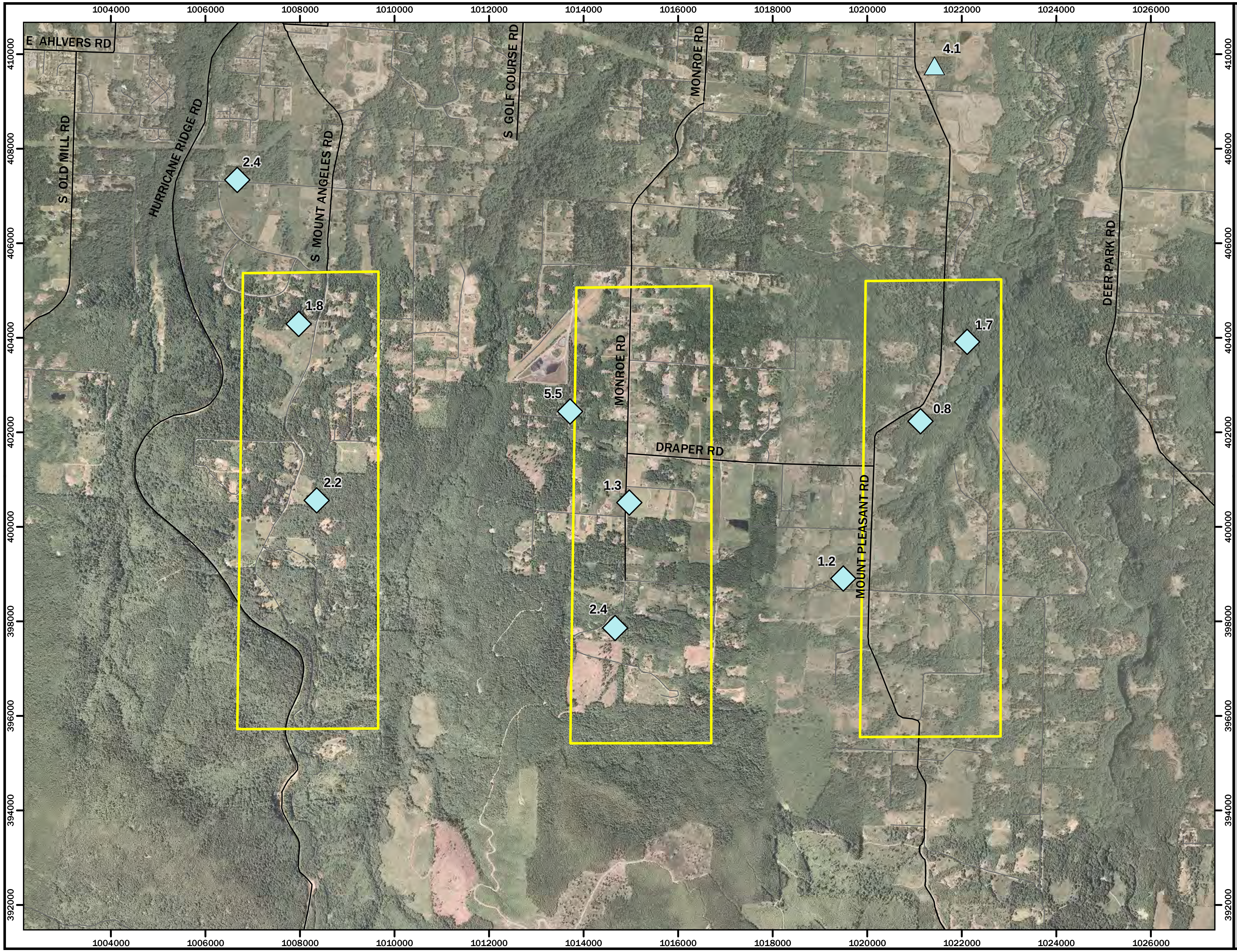
0 600 1,200 2,400
feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (RDR)
Project:
K:/Projects/06-03386-006/Collected_Samples/TEQ_Calc/TEQ Samples Collected in Eastern Zone.mxd

Figure 6-5.
TEQ concentrations in upslope transect areas
Rayonier Mill Off-Property Soil Dioxin Study
Port Angeles, WA



Legend

TEQ (ND=1/2 DL) concentrations shown in ng/kg

- ● 0 to 11
- ● 11 to 20
- ● 20 to 30
- ● > 30

Soil sample type

- △ Forested
- ○ Grid
- □ Highway
- ◇ Transect
- ▭ Upslope transect boundary
- — Arterial or Collector Road
- — Road

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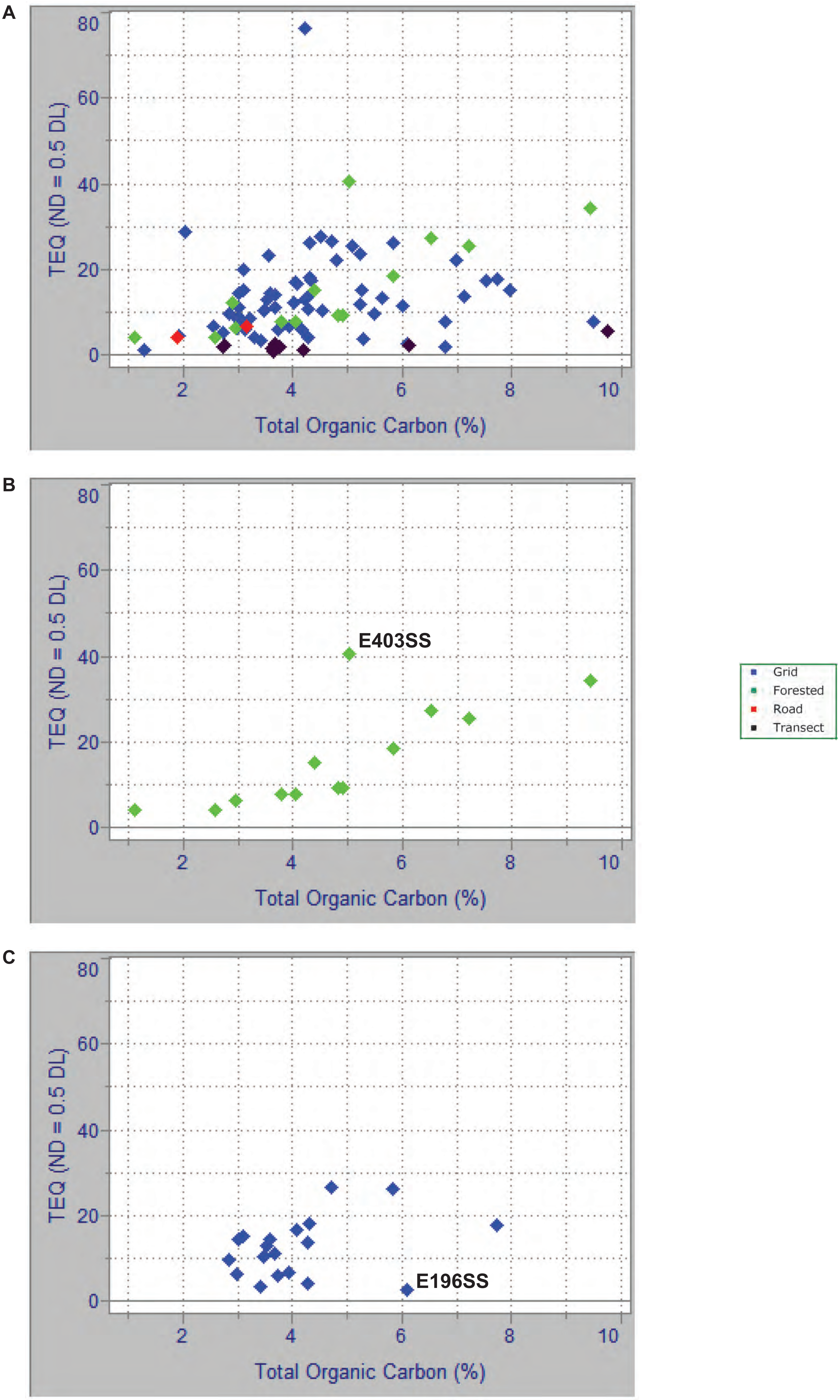
0 1,000 2,000 4,000
feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (RDR)
Project:
K:/Projects/06-03386-006/Collected_Samples/TEQ_Calc/TEQ Samples Collected in Upslope Transects.mxd



Notes: TEQ (ND = 0.5 DL) calculated assuming non-detected congeners present at one-half of the EDL or SDL, as appropriate.
Concentrations are in ng/kg, dry weight.

Figure 6-6 Scatter plots showing TEQs and percent TOC

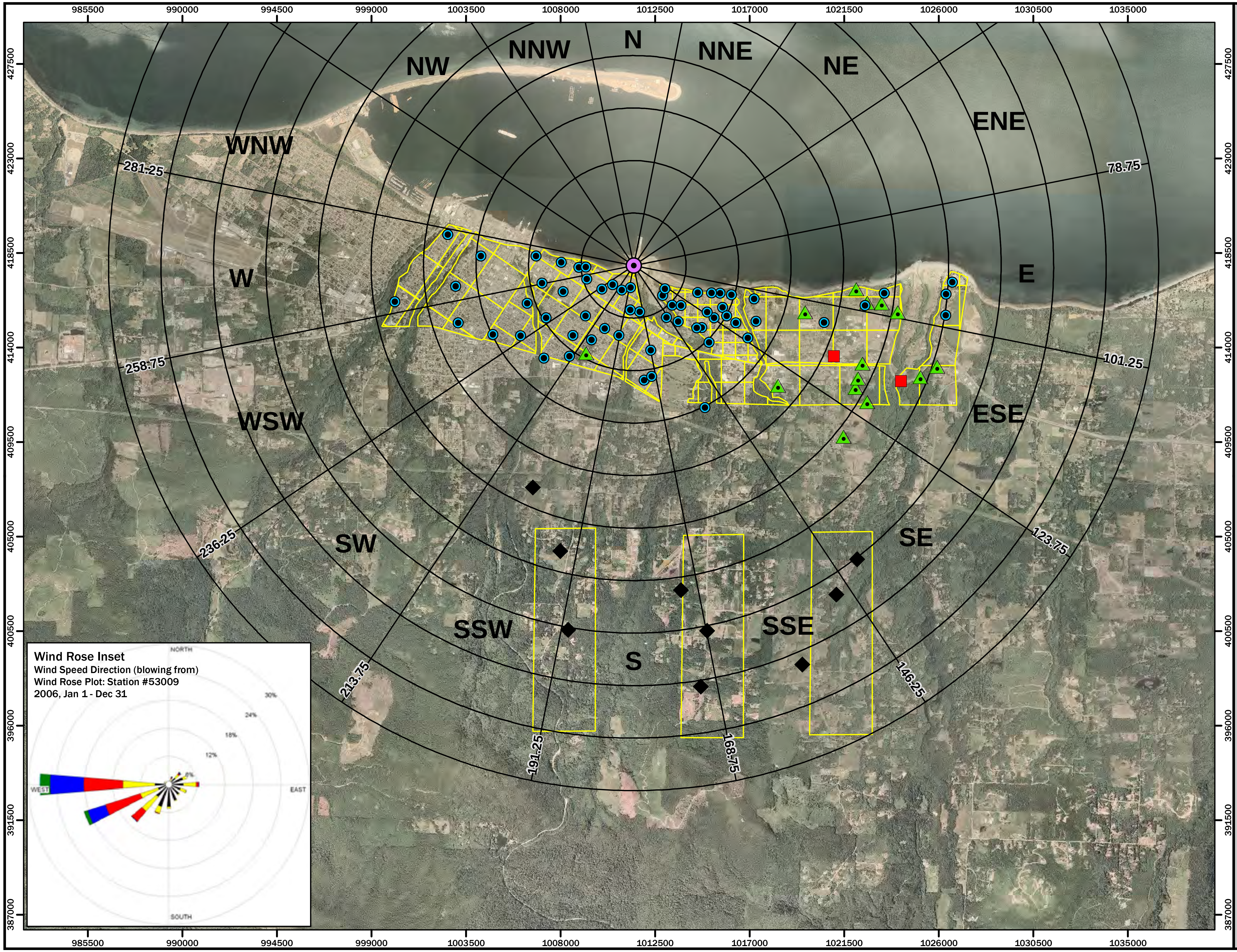


Figure 6-7.
Study area showing sample locations and wind and compass roses with former Rayonier Mill hog fuel boiler as point of origin
Rayonier Mill Off-Property
Soil Dioxin Study
Port Angeles, WA

Legend

▭	Grid cell and/or upslope transect boundary
Collected sample	
▲	Forested
●	Grid
■	Highway
◆	Transect
◉	Former hog fuel boiler
Wind Rose Inset	
Wind speed (knots)	
■	>=22
■	17 to 21
■	11 to 17
■	7 to 11
■	4 to 7
■	1 to 4
	Calms: 0.55%

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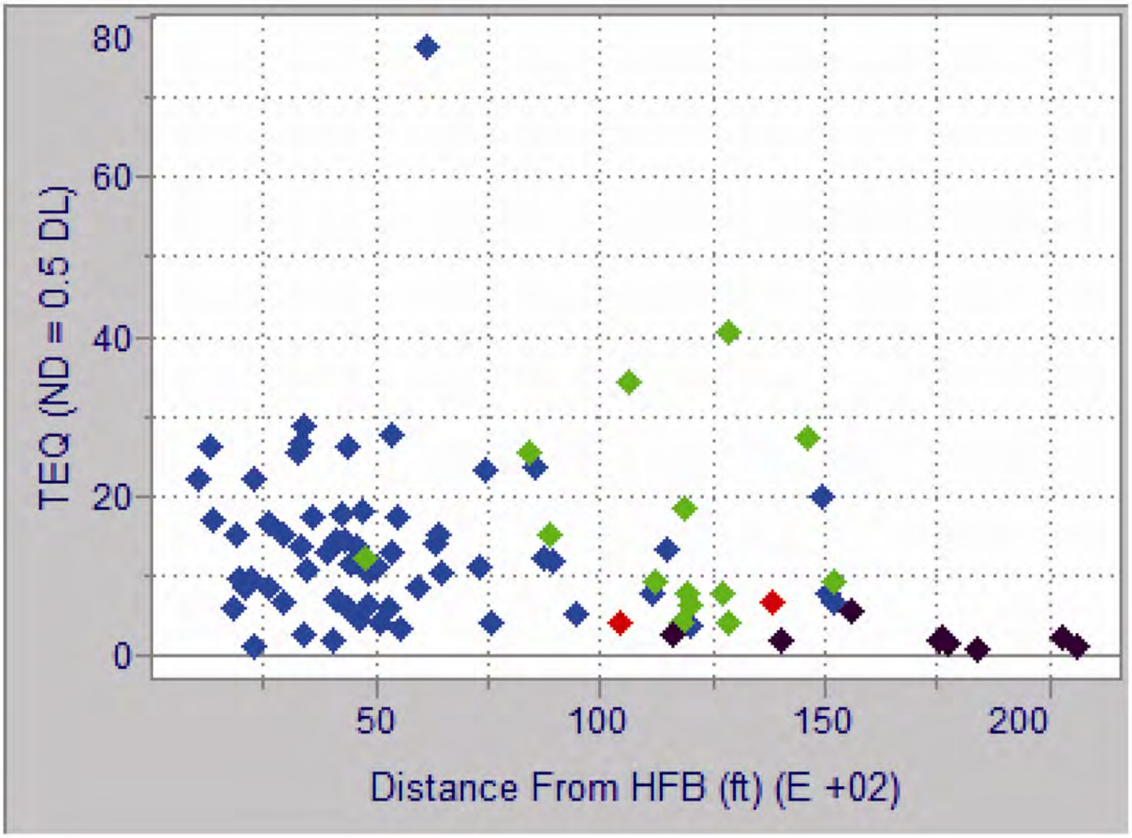
0 2,250 4,500 9,000
Feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (RDR)
Project:
K:/Projects/06-03386-006/Projects/Compass Rose Report.mxd



Notes:
TEQ (ND = 0.5 DL) calculated assuming nondetected congeners present at one-half of the EDL or SDL, as appropriate.
Concentrations are in ng/kg, dry weight.
Distance is in hundreds of feet from the former hog fuel boiler (HFB).

Key:

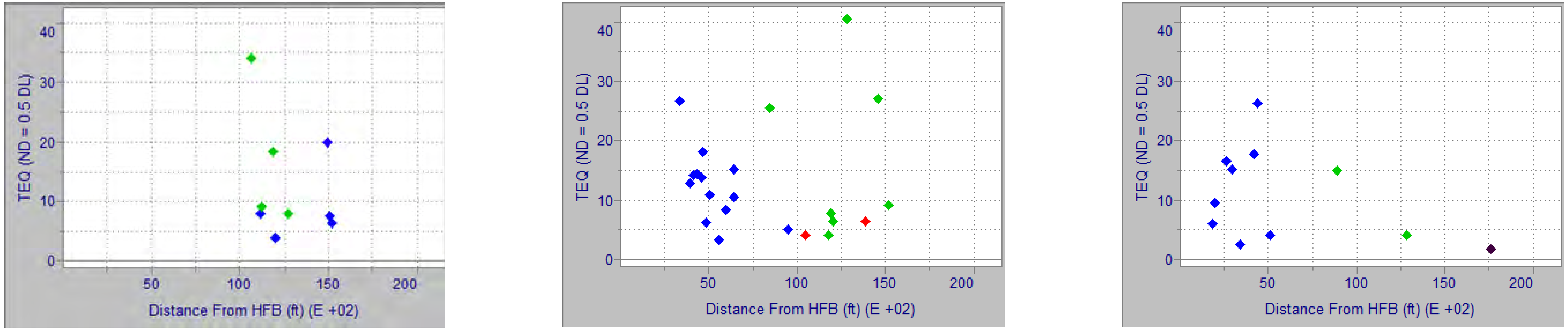
◆ = Grid sample

◆ = Upslope transect sample

◆ = Roadside sample

◆ = Forested sample

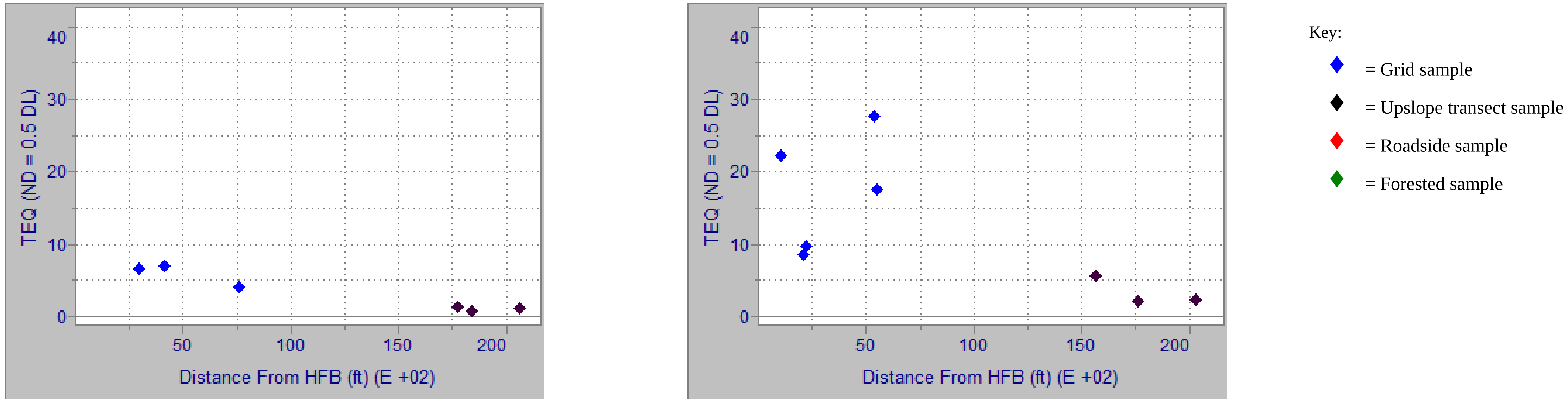
Figure 6-8 Scatter plot showing TEQ concentrations and distance of samples from the former Rayonier Mill hog fuel boiler



East Wind Sector

East-Southeast Wind Sector

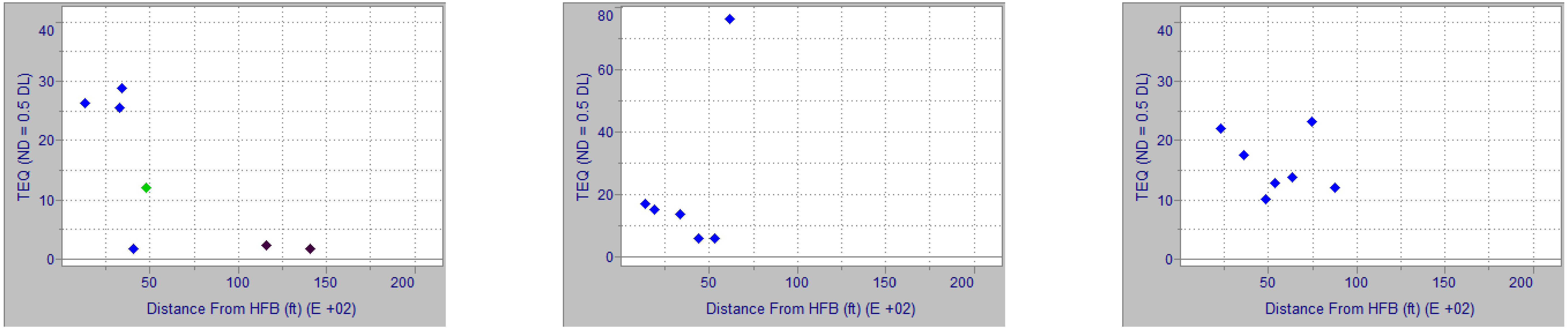
Southeast Wind Sector



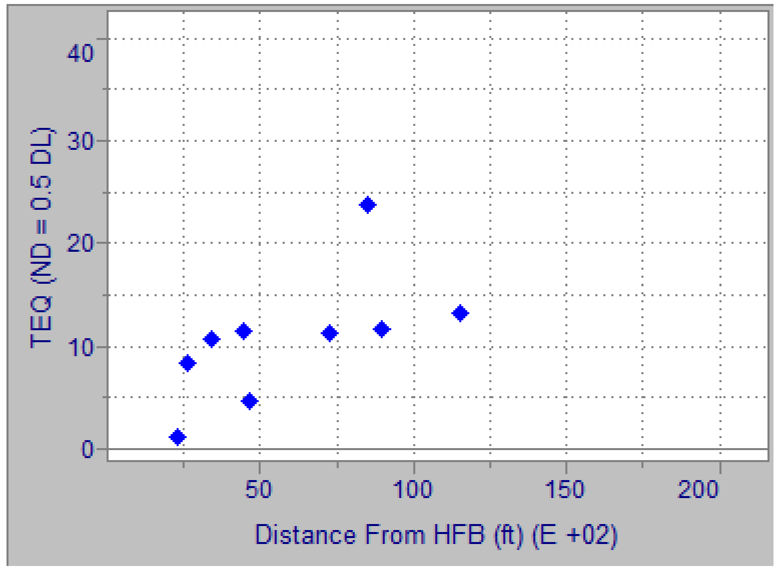
South-Southeast Wind Sector

South Wind Sector

Figure 6-9 Scatter plots showing TEQ concentrations and distance by wind sector



South-Southwest Wind Sector **Southwest Wind Sector** **West-Southwest Wind Sector**



West Wind Sector

Key:

◆ = Grid sample

◆ = Upslope transect sample

◆ = Roadside sample

◆ = Forested sample

Figure 6-9 (continued) Scatter plots showing TEQ concentrations and distance by wind sector

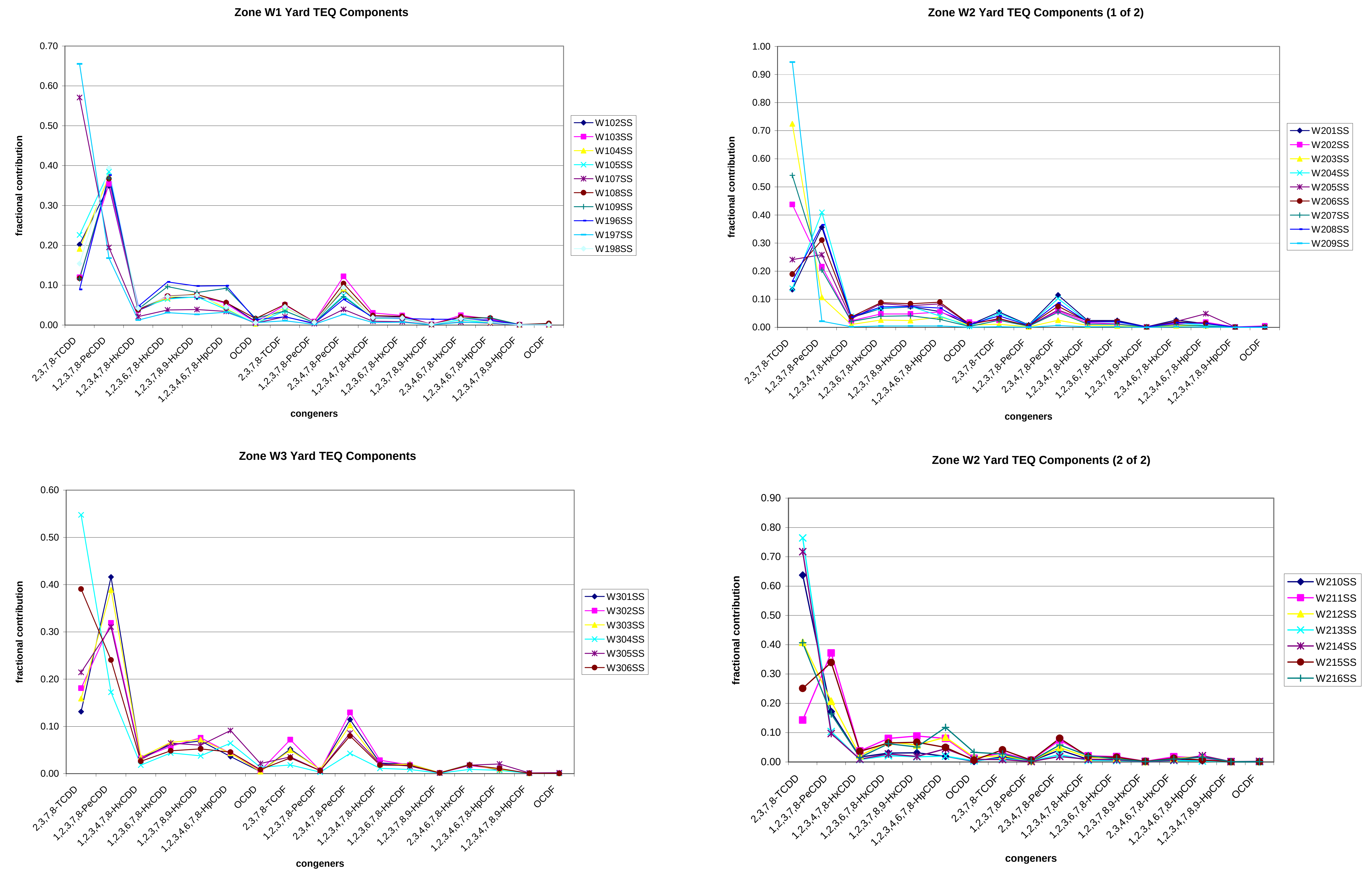
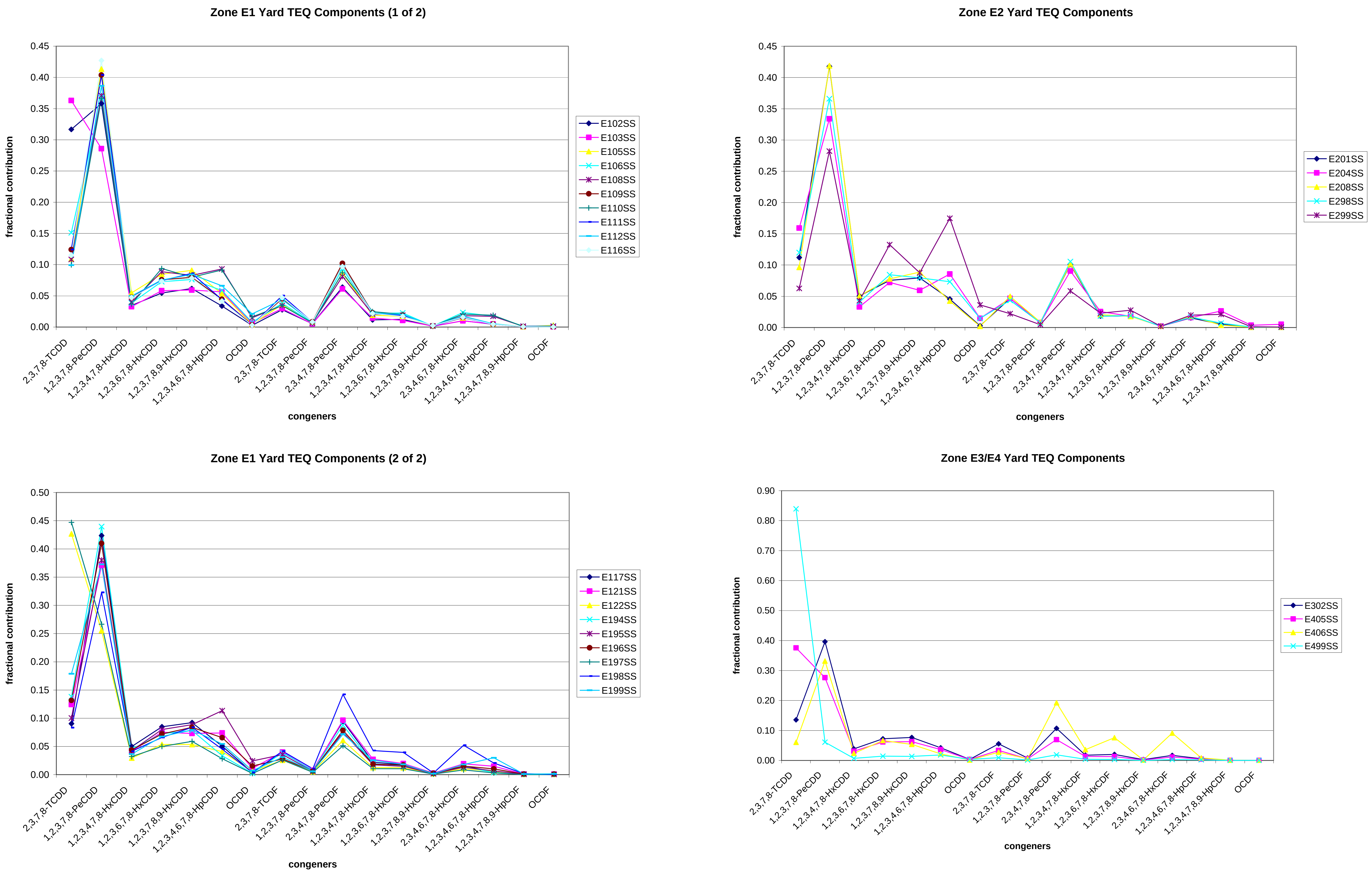


Figure 6-10 Line plots showing fractional contributions of congeners to TEQ results


Zone E1 Yard TEQ Components (1 of 2)

Zone E2 Yard TEQ Components

Zone E1 Yard TEQ Components (2 of 2)

Zone E3/E4 Yard TEQ Components

Figure 6-10 (continued) Line plots showing fractional contributions of congeners to TEQ results

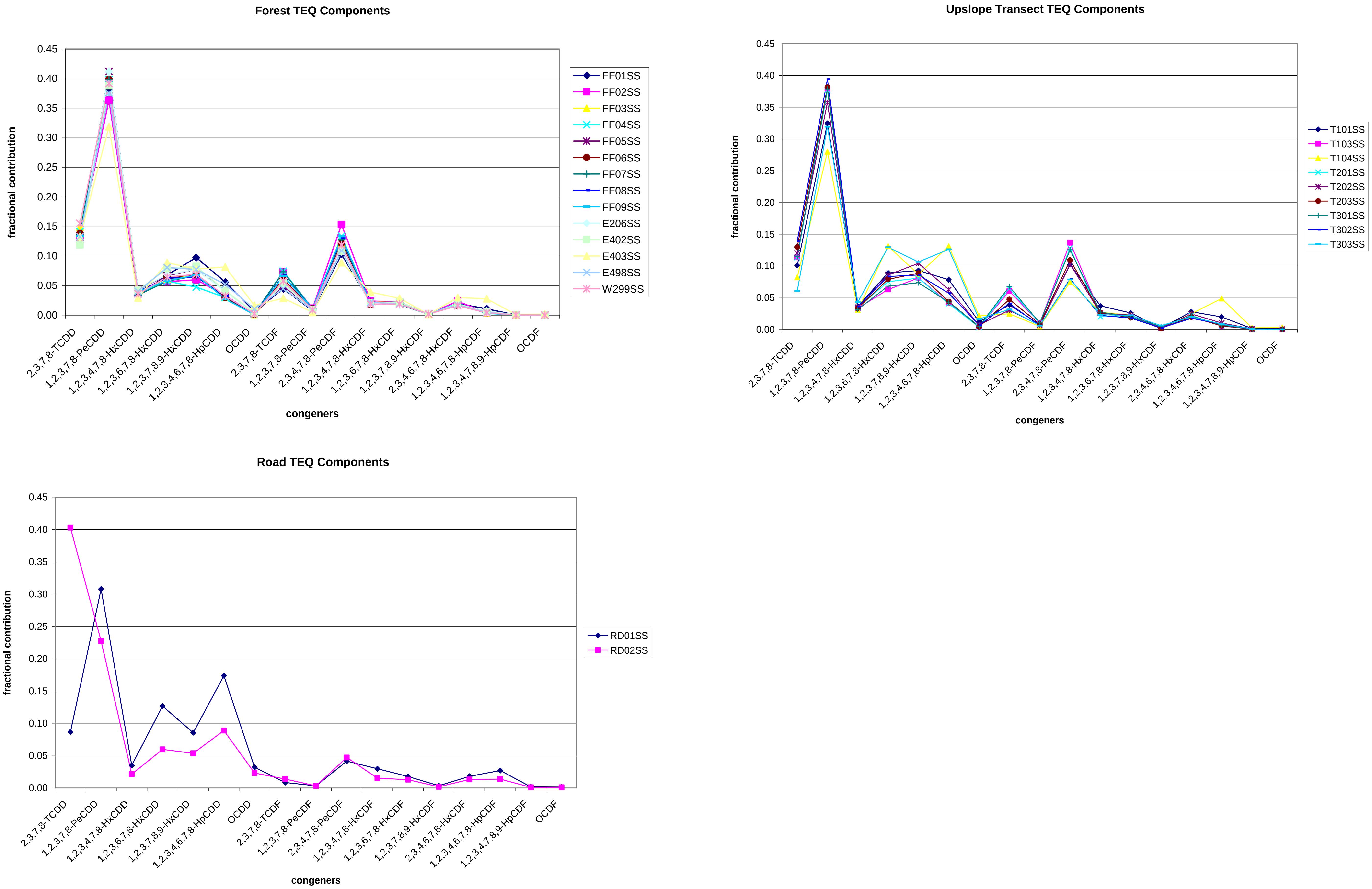


Figure 6-10 (continued) Line plots showing fractional contributions of congeners to TEQ results

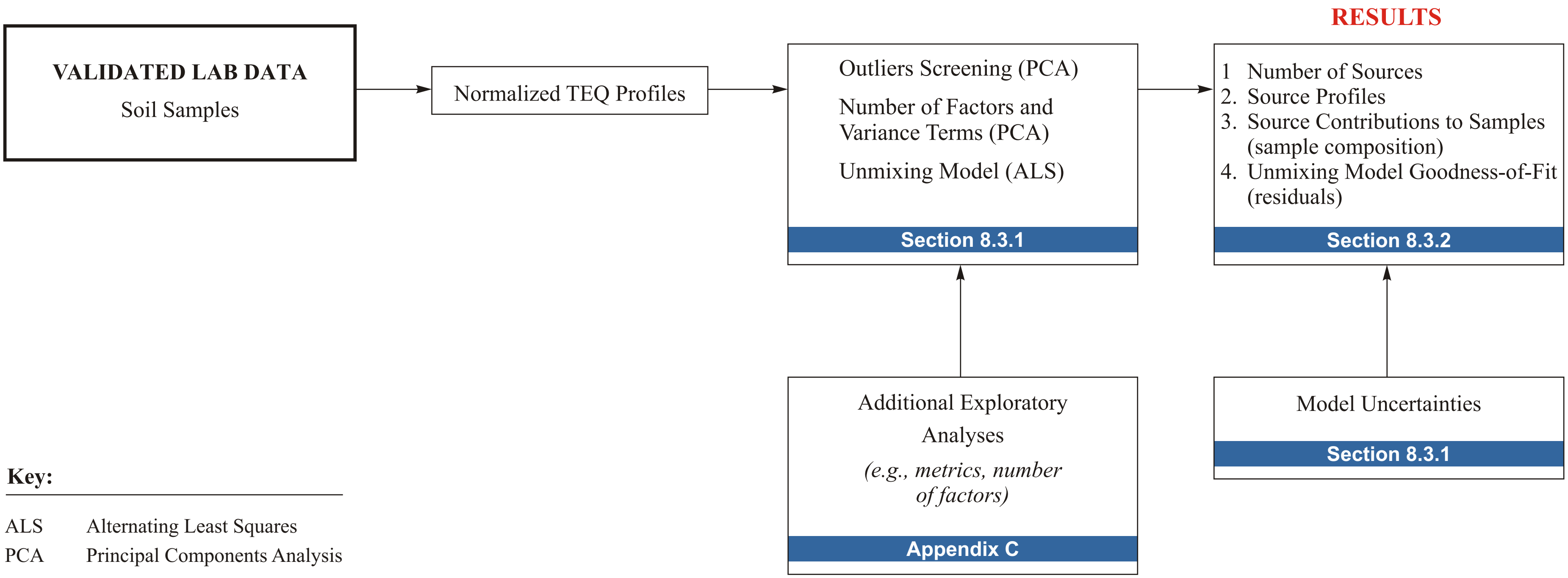


Figure 7-1 Chemometric analysis schematic

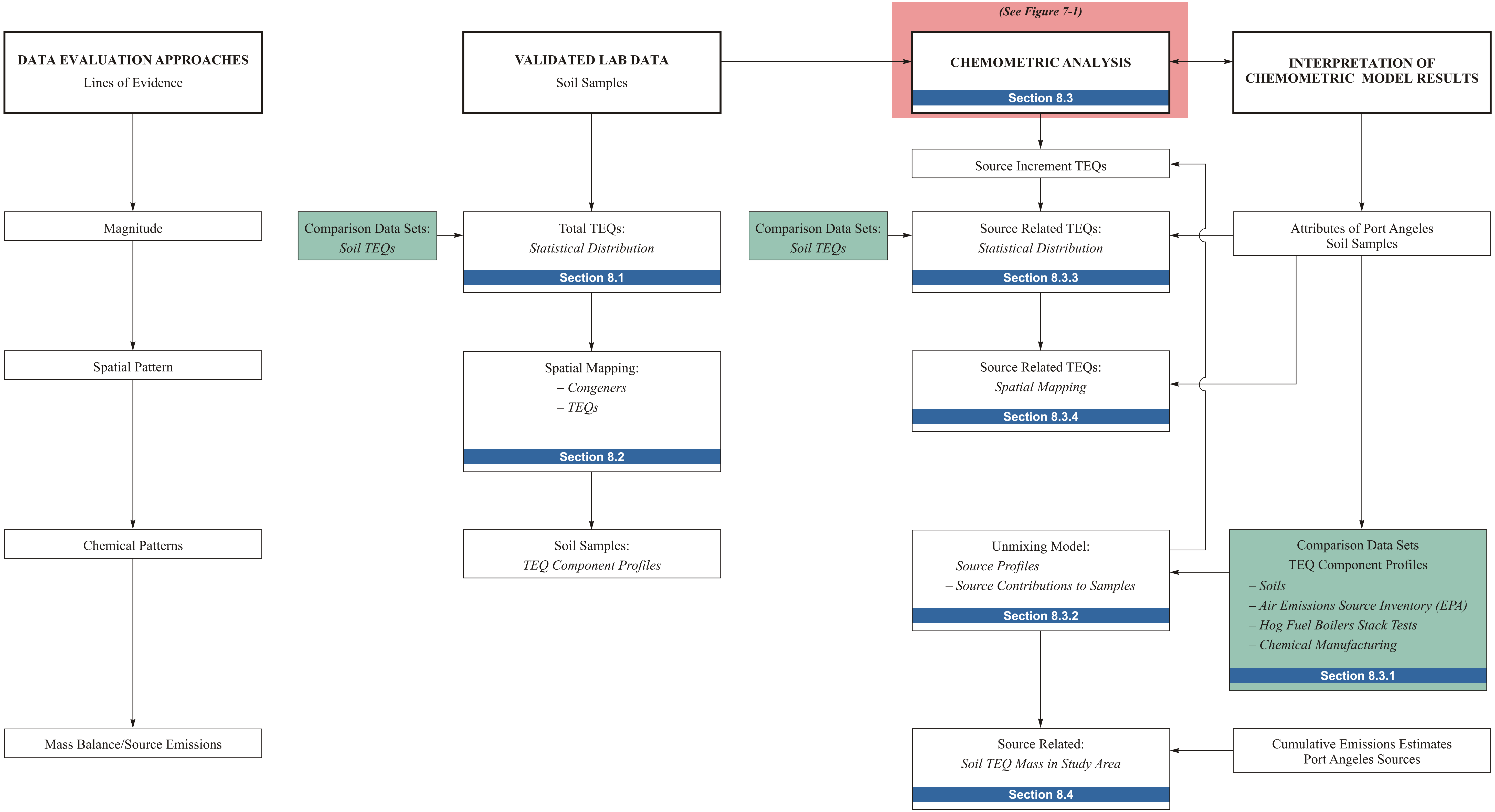


Figure 7-2 Data evaluations: overview

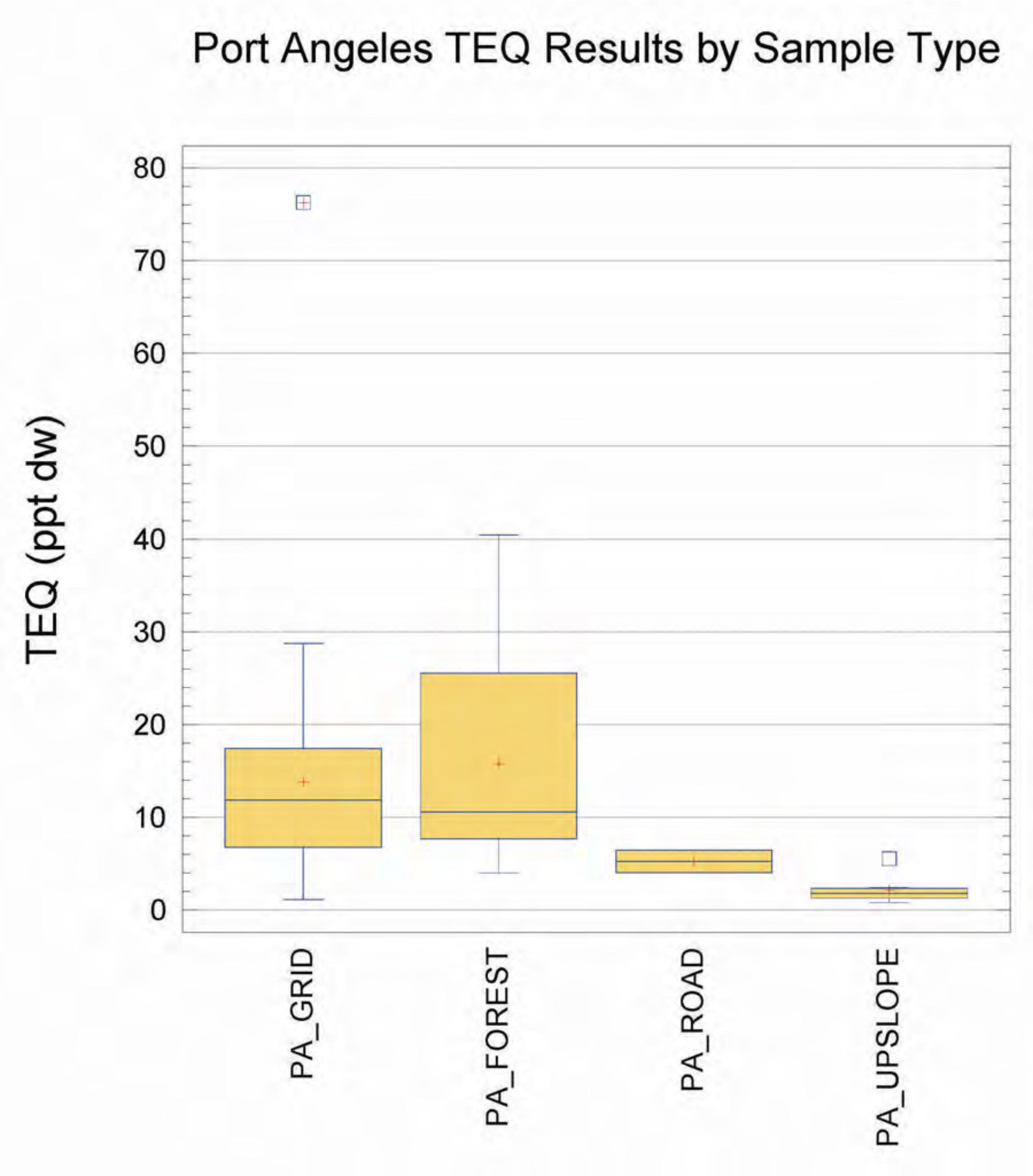


Figure 8-1 Port Angeles soil samples: comparison of TEQs by sample type

Note: For a description of Box-and-Whisker plots, refer to the text box included in Section 8.1.

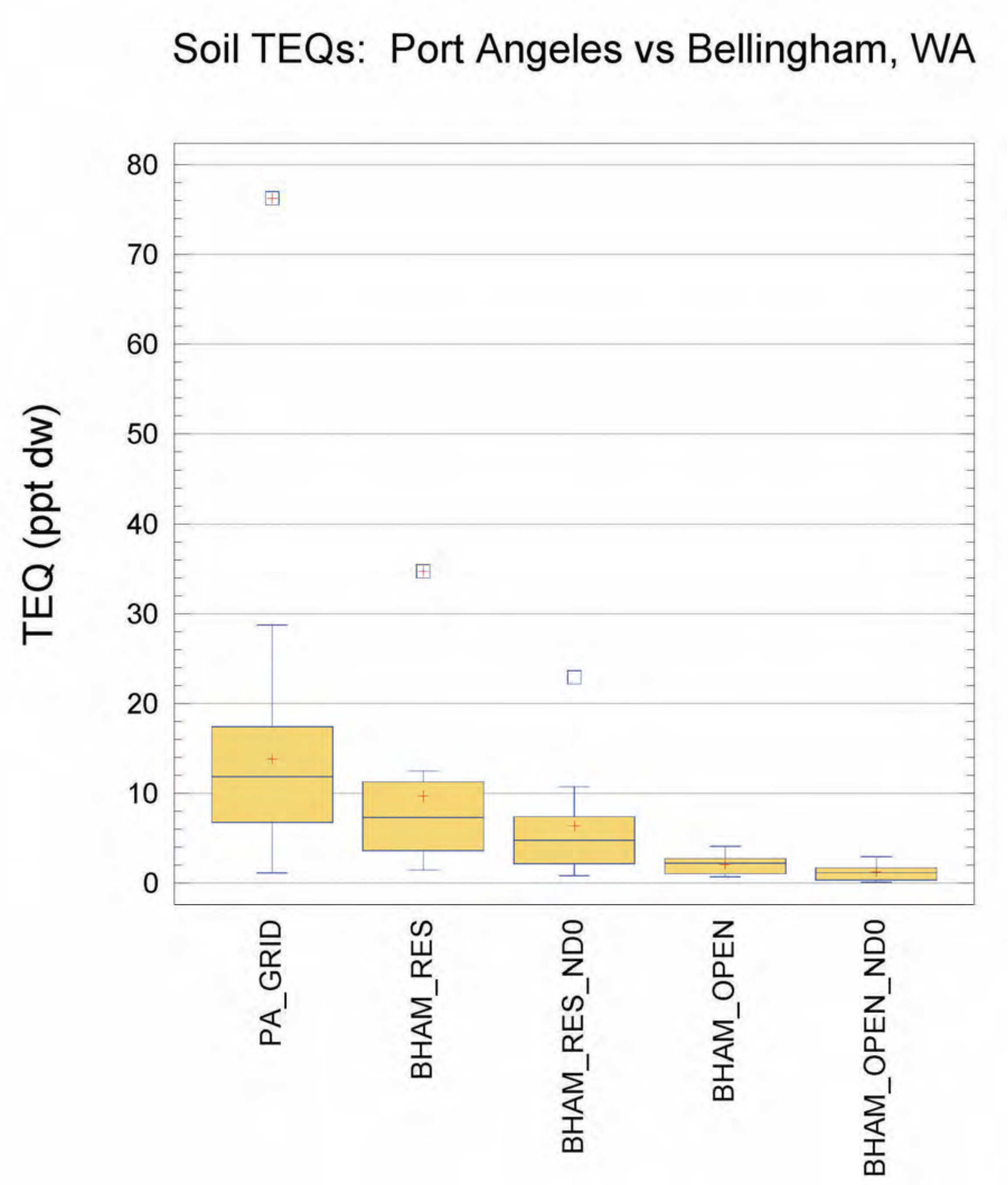


Figure 8-2 Comparison of soil TEQs: Port Angeles versus Bellingham, WA

Note: For a description of Box-and-Whisker plots, refer to the text box included in Section 8.1.

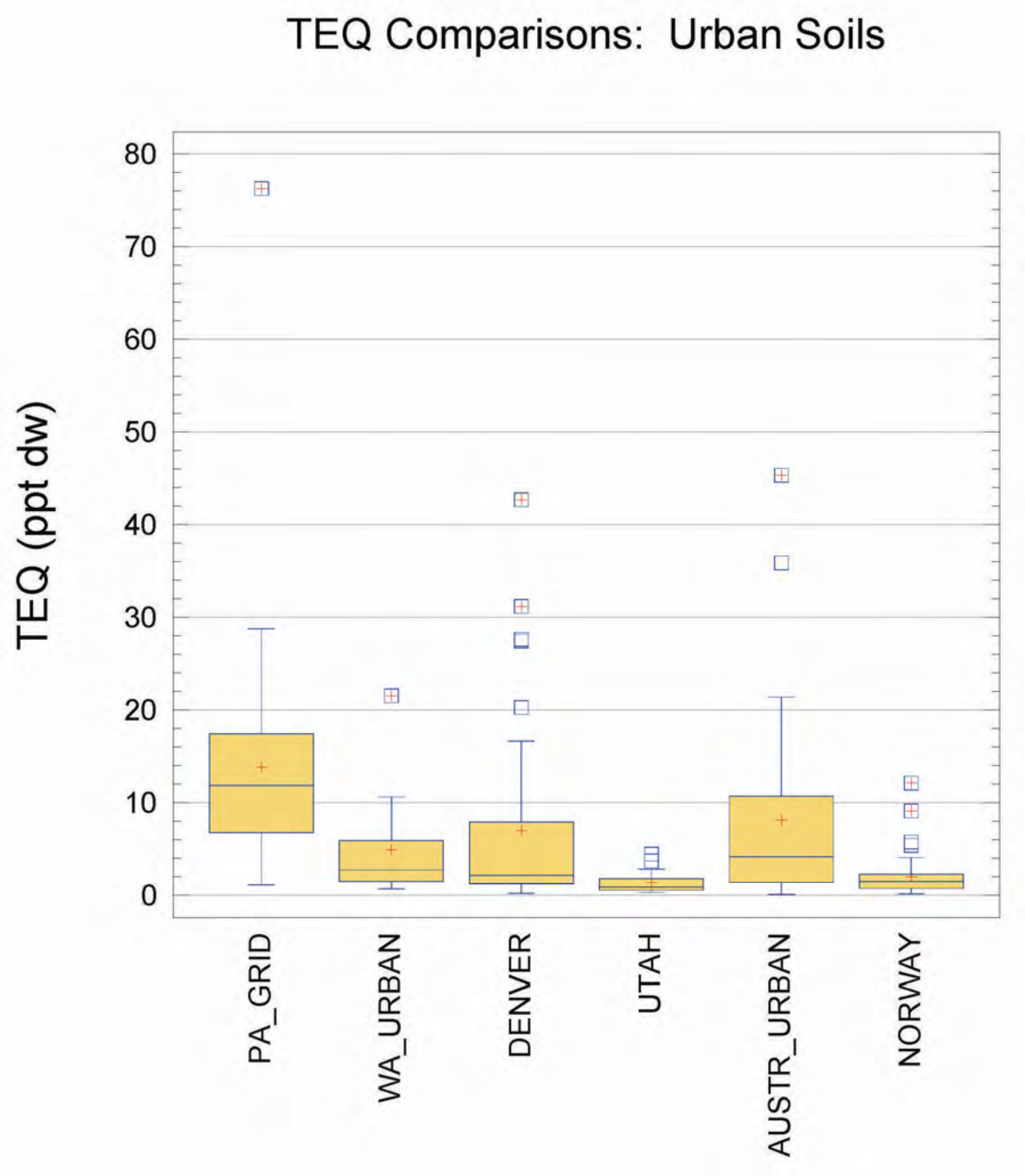


Figure 8-3 Comparison of soil TEQs: Port Angeles versus urban soils

Note: For a description of Box-and-Whisker plots, refer to the text box included in Section 8.1.

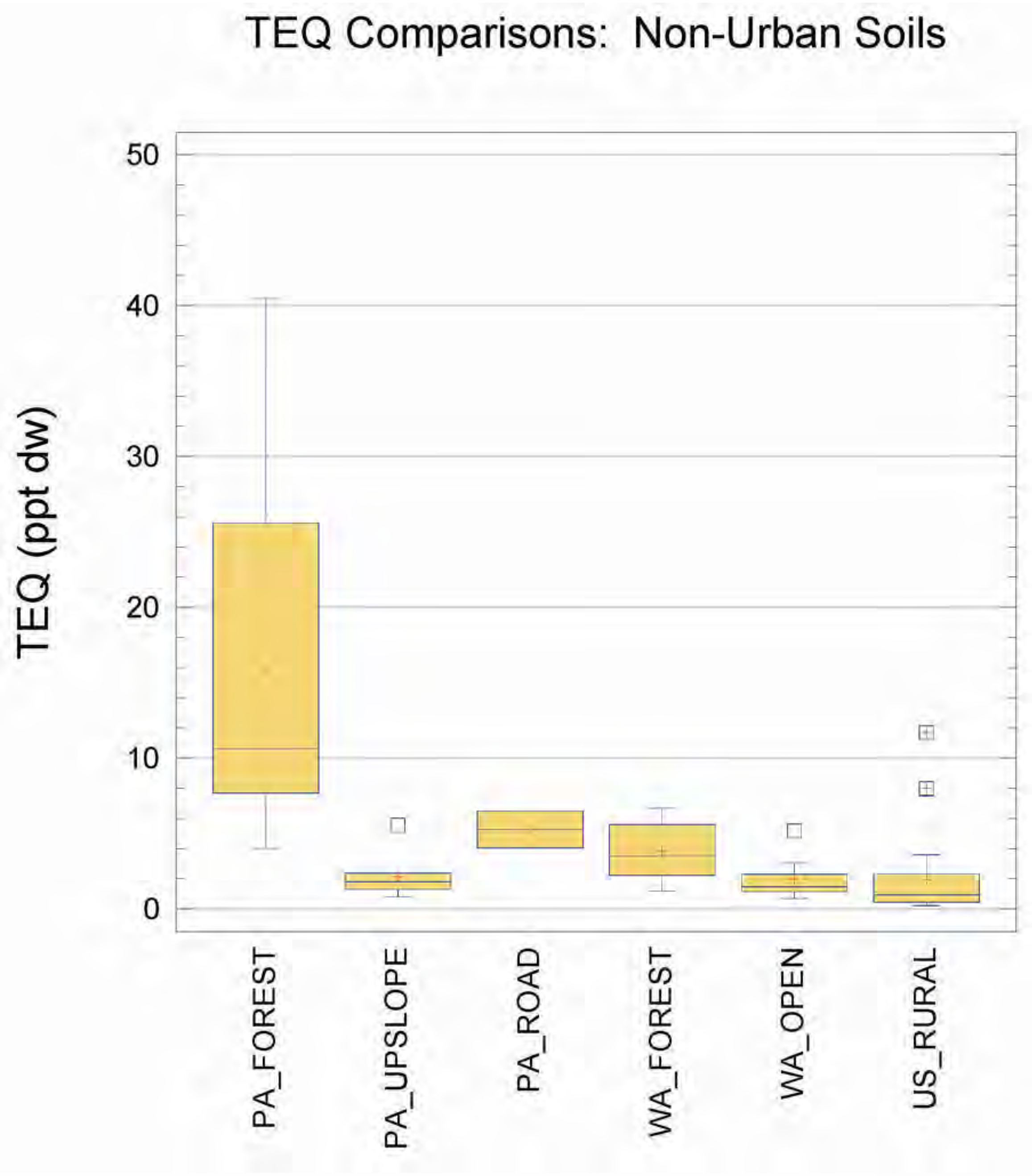


Figure 8-4 Comparison of soil TEQs: Port Angeles versus non-urban soils

Note: For a description of Box-and-Whisker plots, refer to the text box included in Section 8.1.

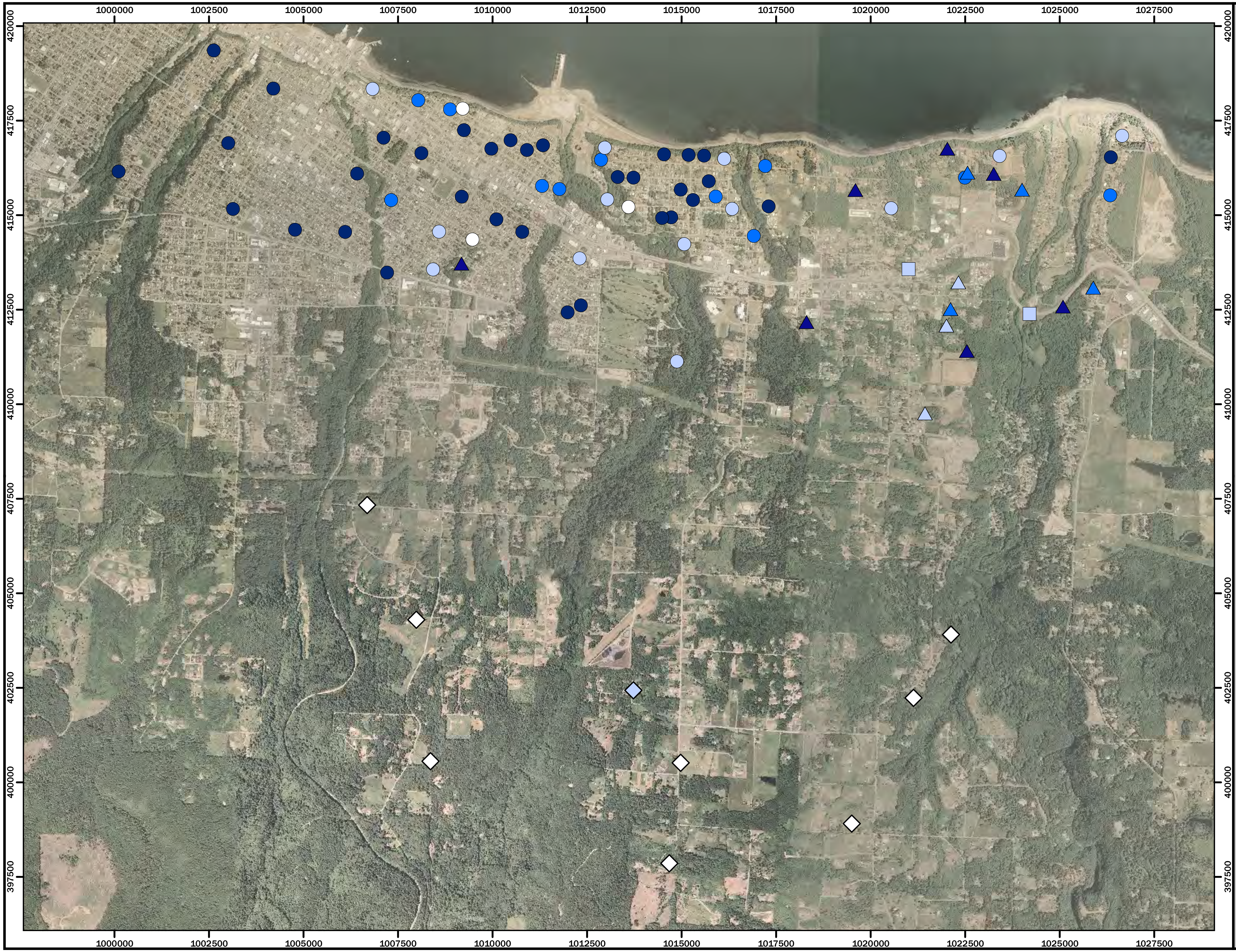


Figure 8-5.
Total TEQs
Rayonier Mill Off-Property
Soil Dioxin Study
Port Angeles, WA

Legend

TEQ (ND = 1/2 DL) concentrations shown in ng/kg

- ○ 0 to 3
- ● 3 to 7
- ● 7 to 11
- ● > 11

Soil sample type

- △ Forested
- ○ Grid
- □ Highway
- ◇ Transect

Note: Contour plots used in these data evaluations cannot predict values at unsampled locations. Rather, they help visualize the large-scale distribution of the Port Angeles soils data. Local variability in dioxin/furan concentrations may be high and is likely to reflect individual property histories.

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0 1,250 2,500 5,000
feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (RDR)
Project:
K:\Projects\06-03386-006\Collected_Samples\TEQ_Calc\TEQ Increment Grid Dots and Contours.mxd

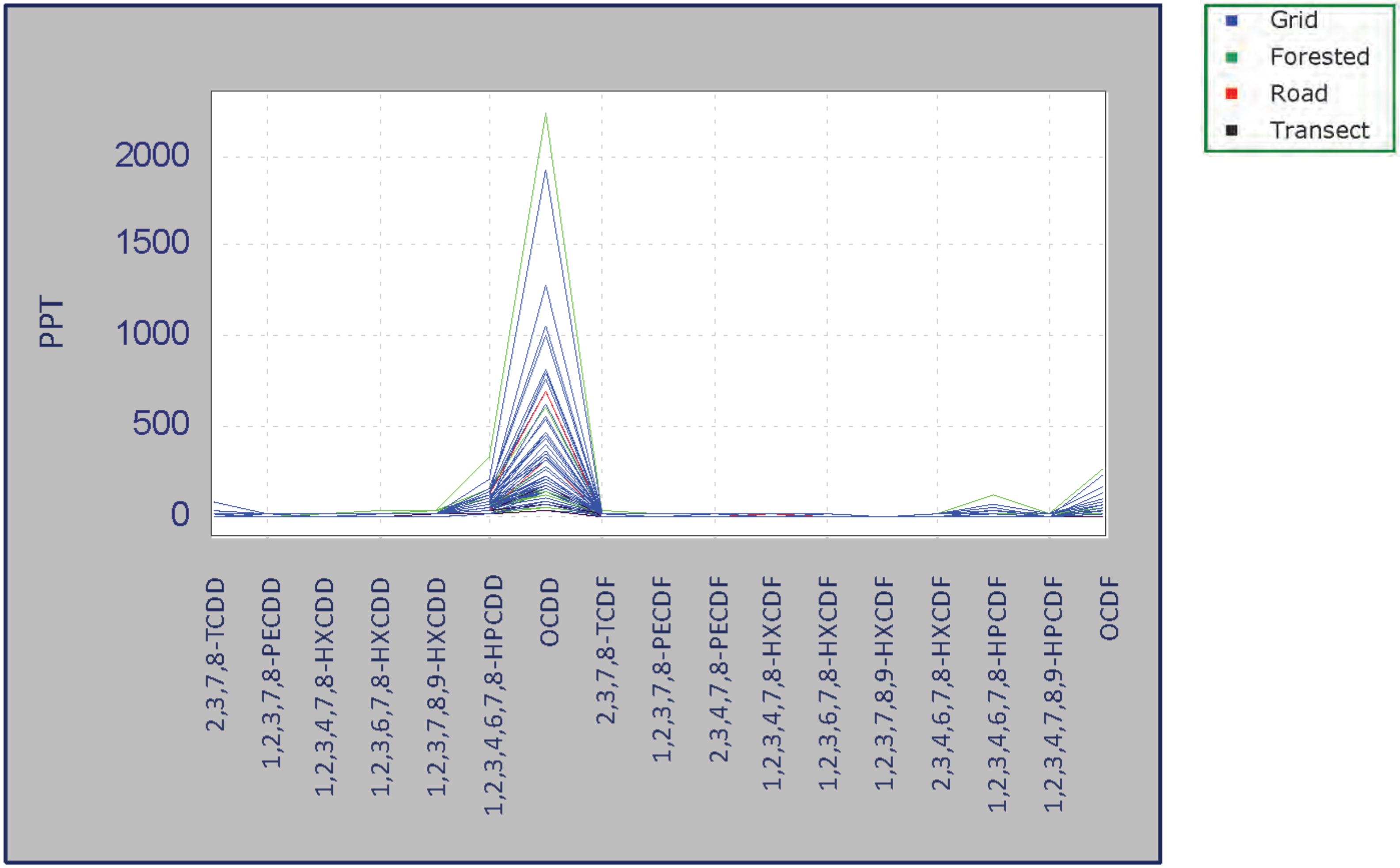


Figure 8-6 Port Angeles samples: bulk congener profiles

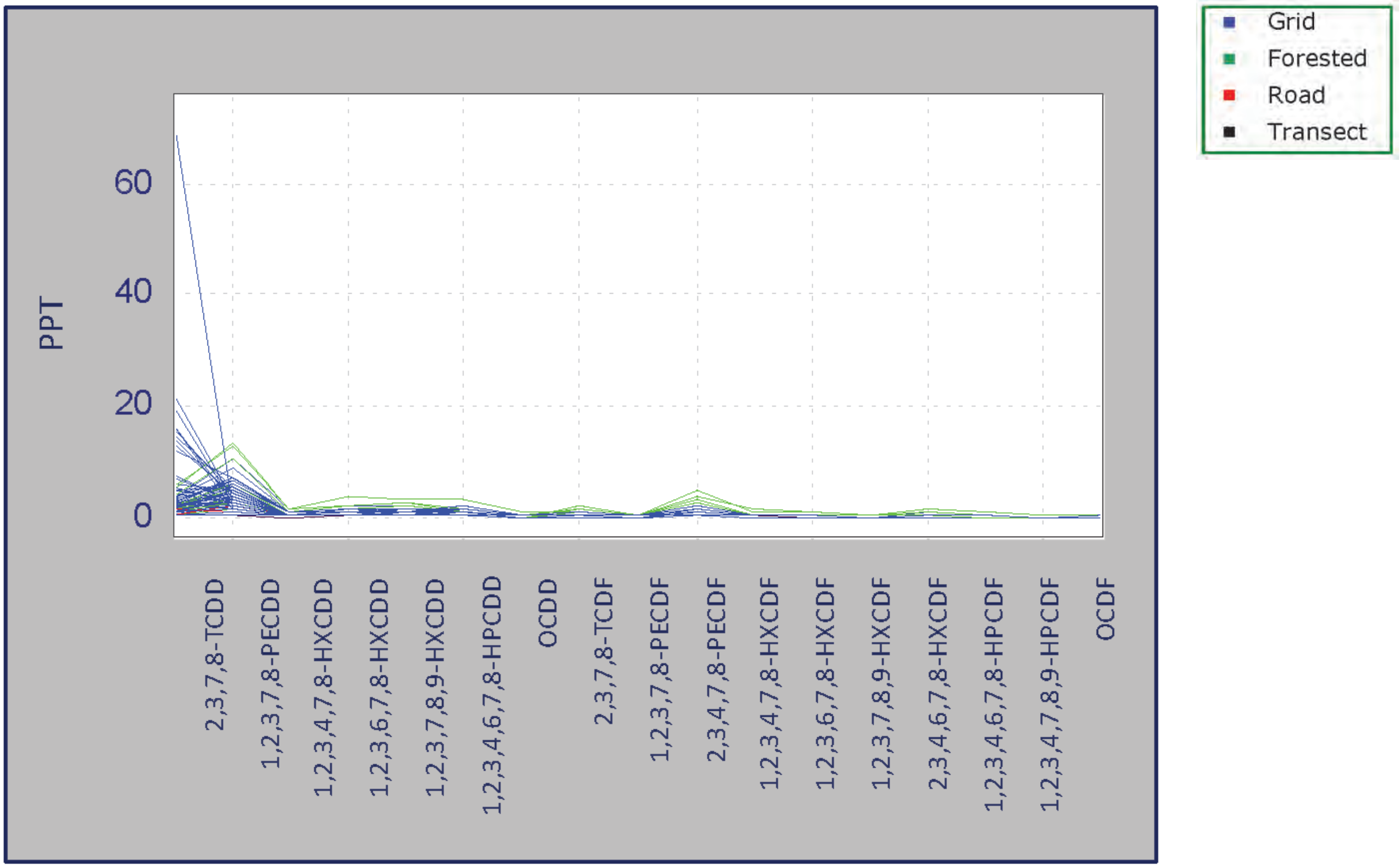


Figure 8-7 Port Angeles samples: TEQ profiles

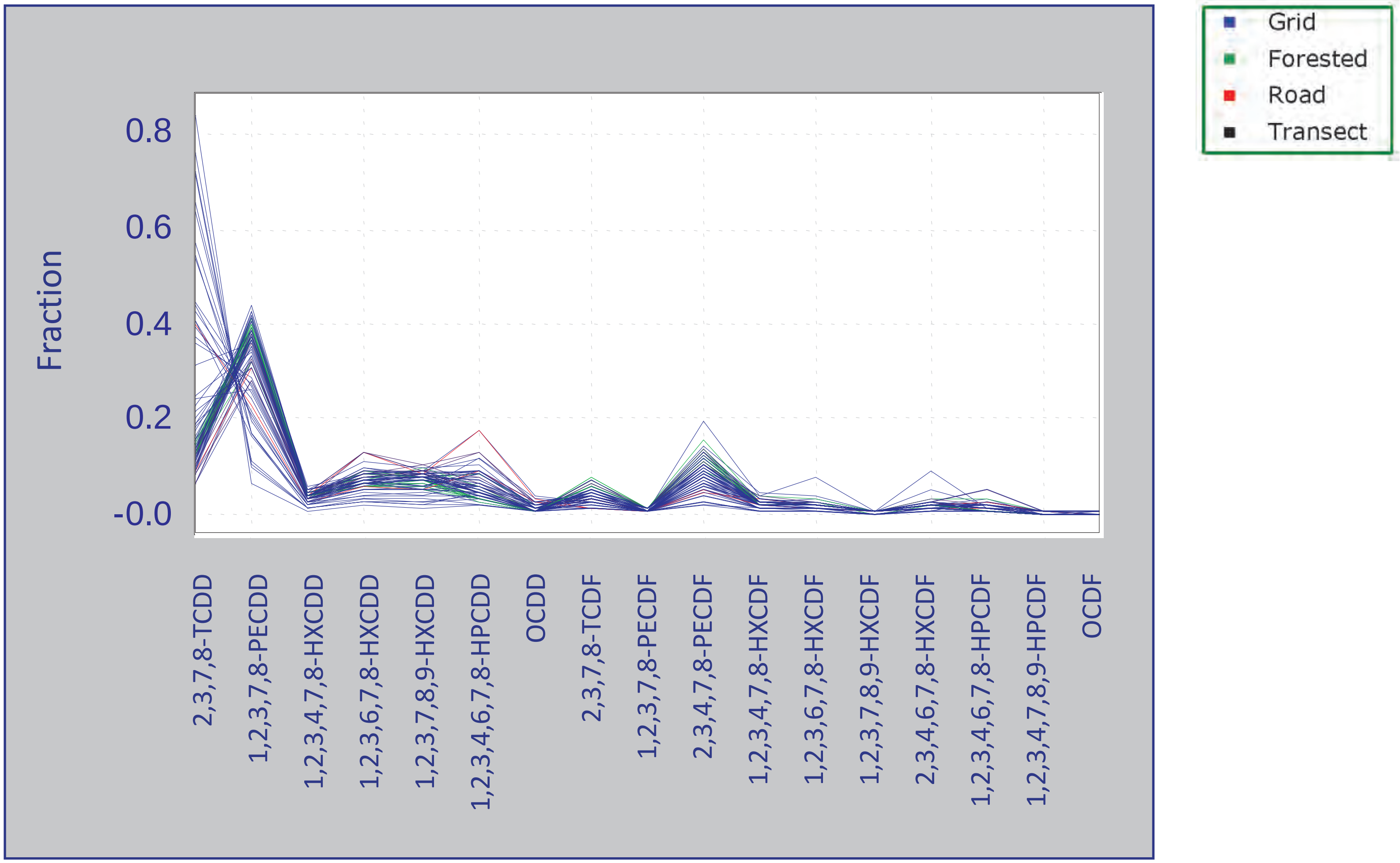


Figure 8-8 Port Angeles soil samples: normalized TEQ profiles

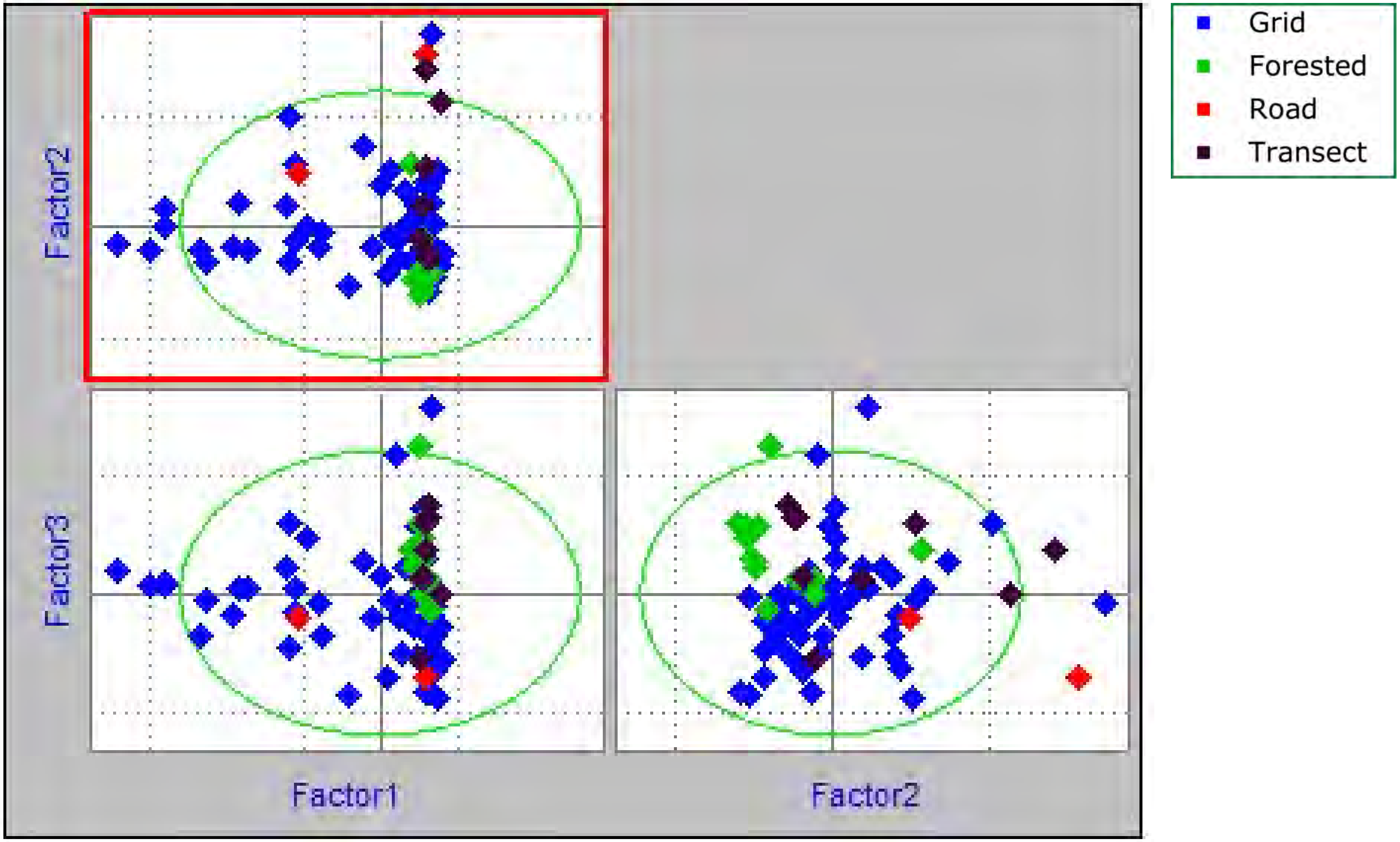


Figure 8-9 Port Angeles soil samples: PCA plot

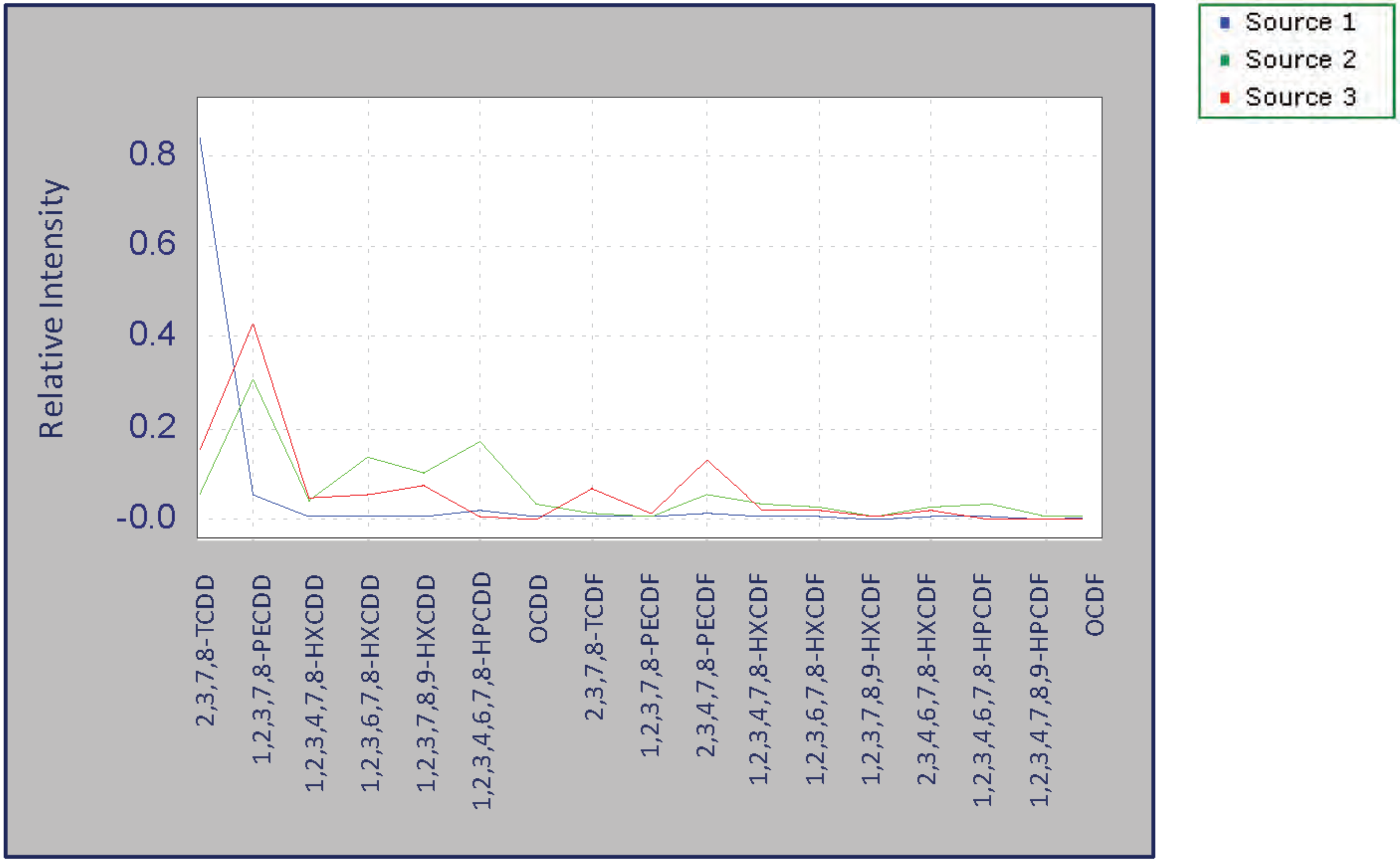


Figure 8-10 Unmixing model source profiles

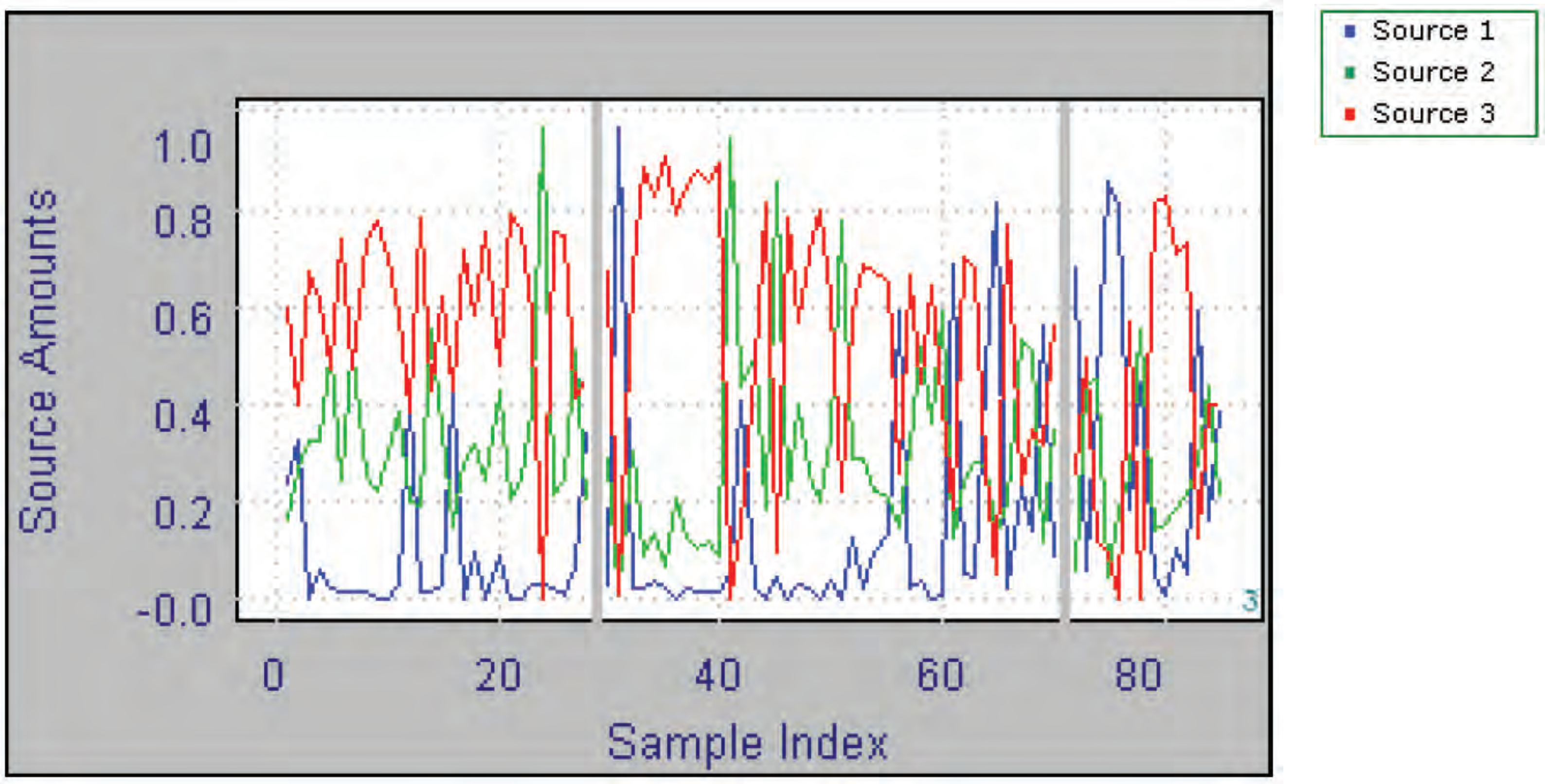


Figure 8-11 Unmixing model source contribution to samples

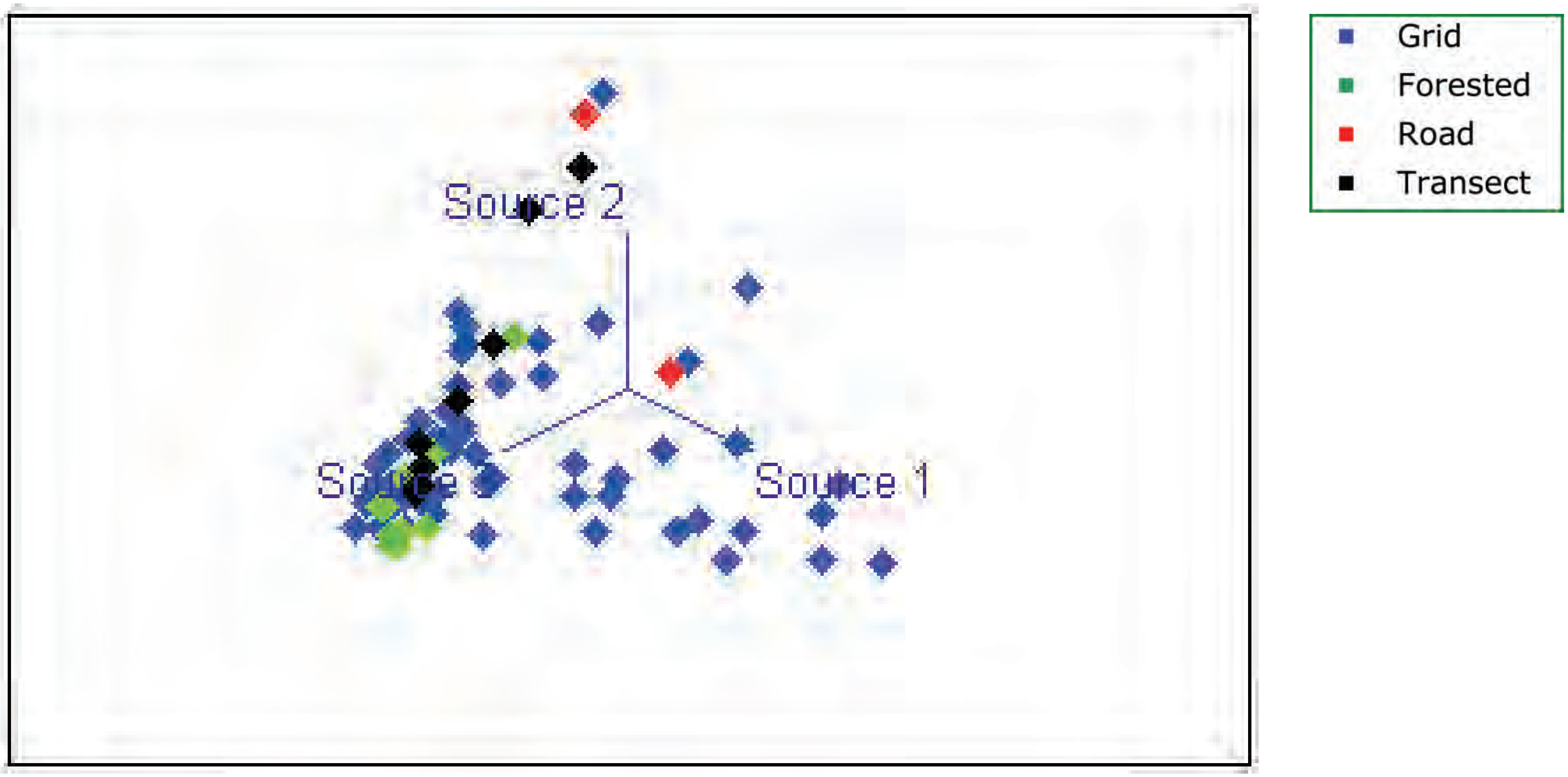


Figure 8-12 Ternary plot of sample compositions

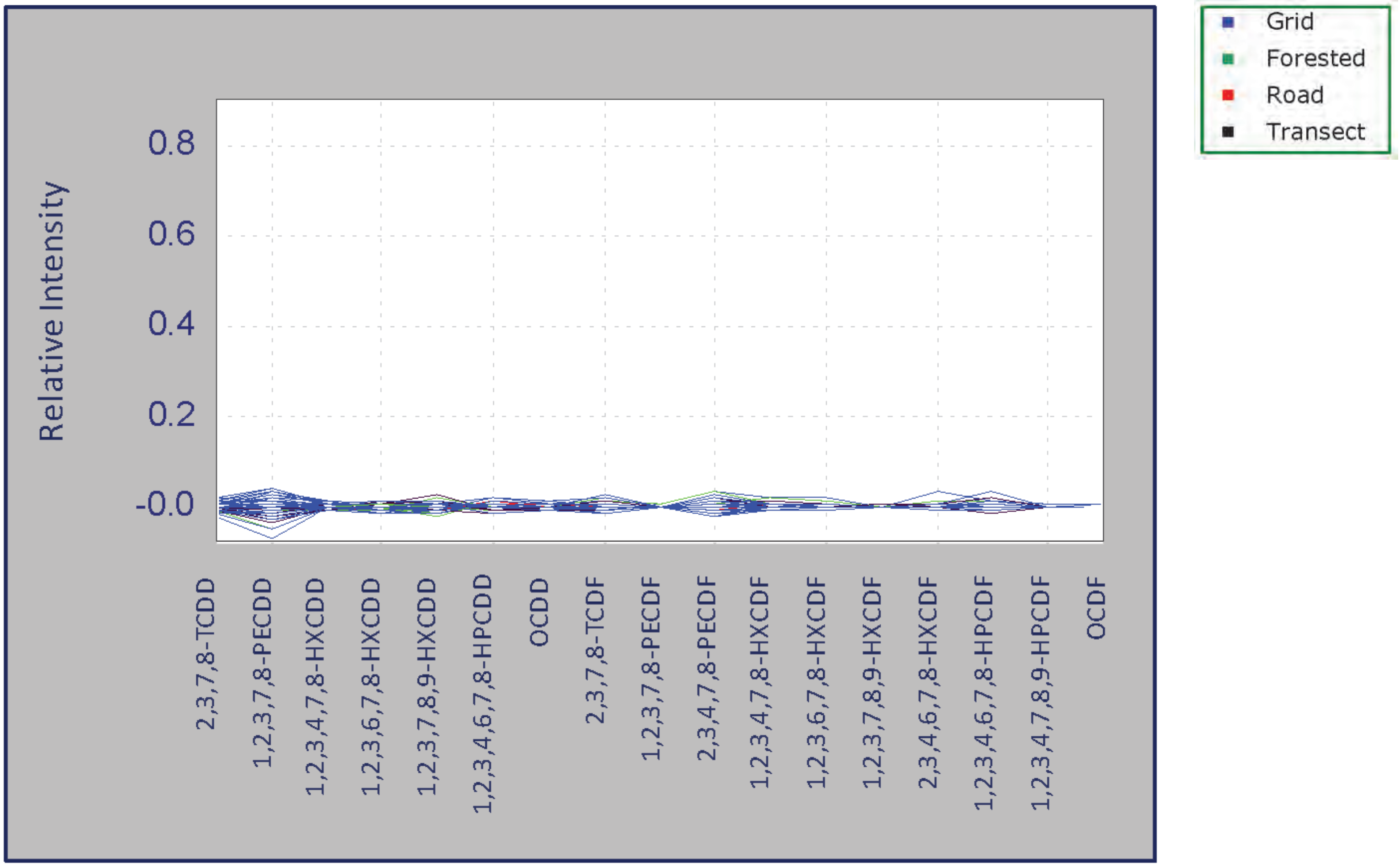
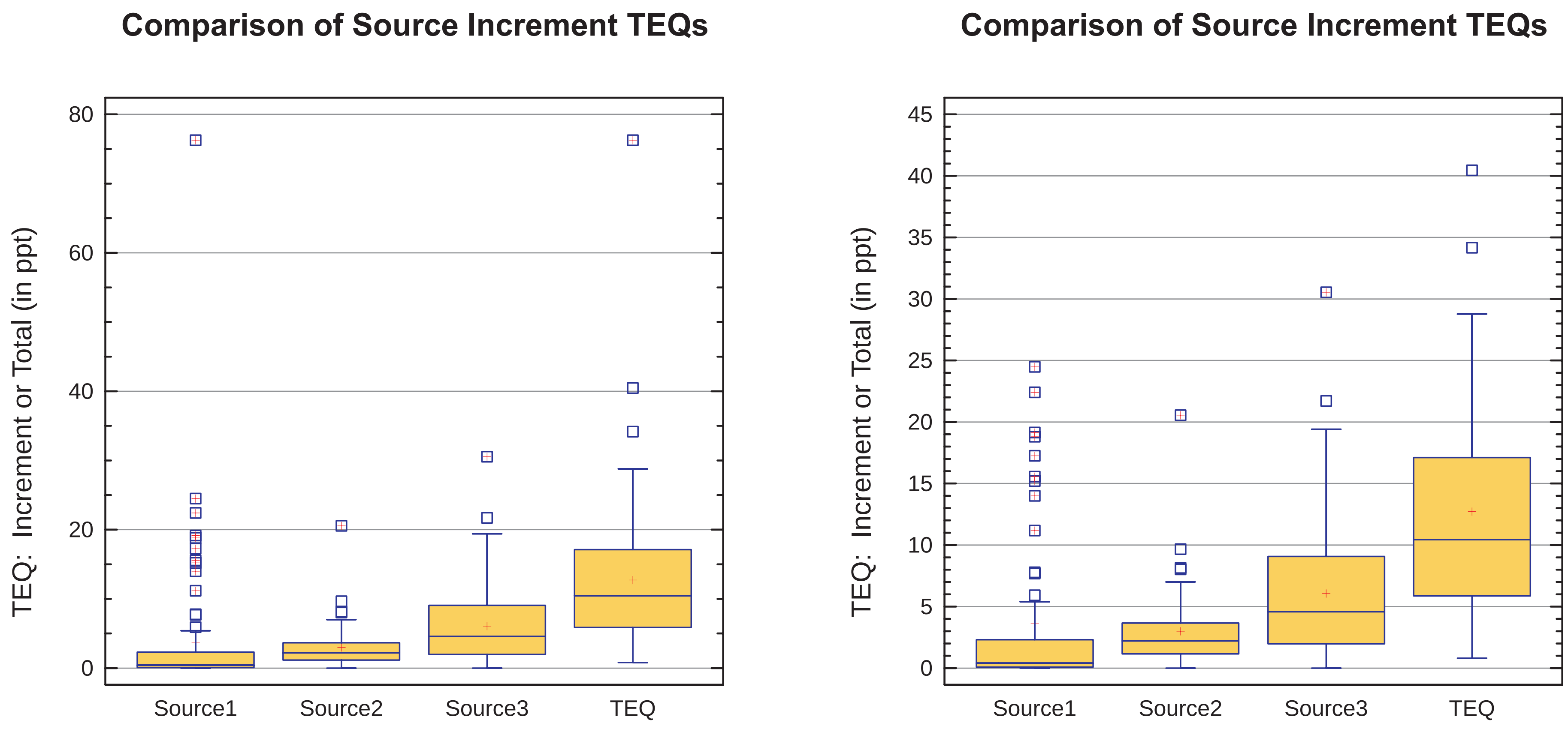
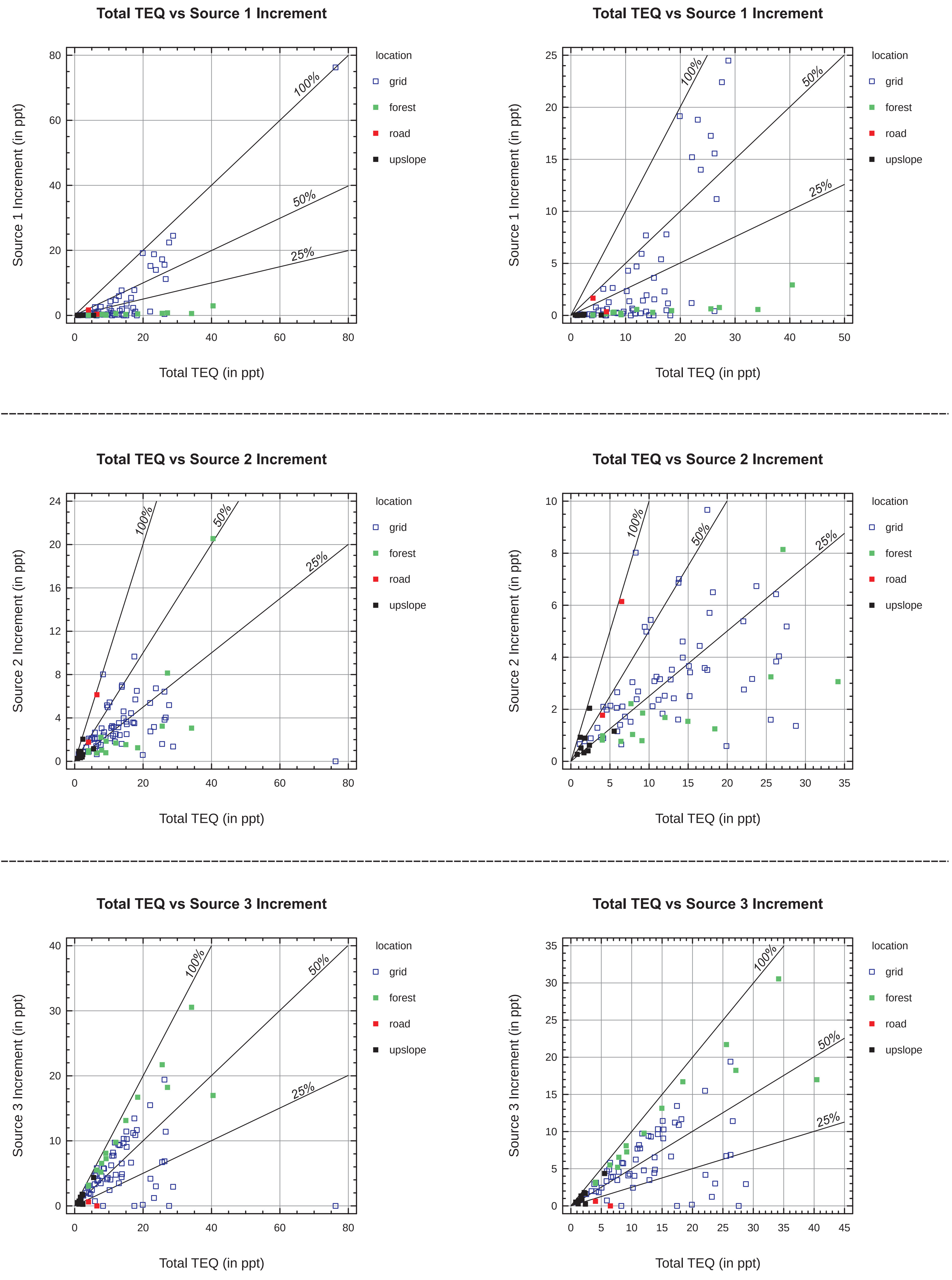


Figure 8-13 Unmixing model residuals



Note: Box-and-Whisker plot on right omits one high outlier value from the plot and rescales the vertical axis, to provide a clearer comparison.

Figure 8-14 Comparison of source increment contributions to total TEQ



Note: Scatter plots in right hand column omit one or two high outlier values and rescale the axes to better show patterns for the bulk of the data points.

Figure 8-15 Scatter plots showing source increment contributions to total TEQ

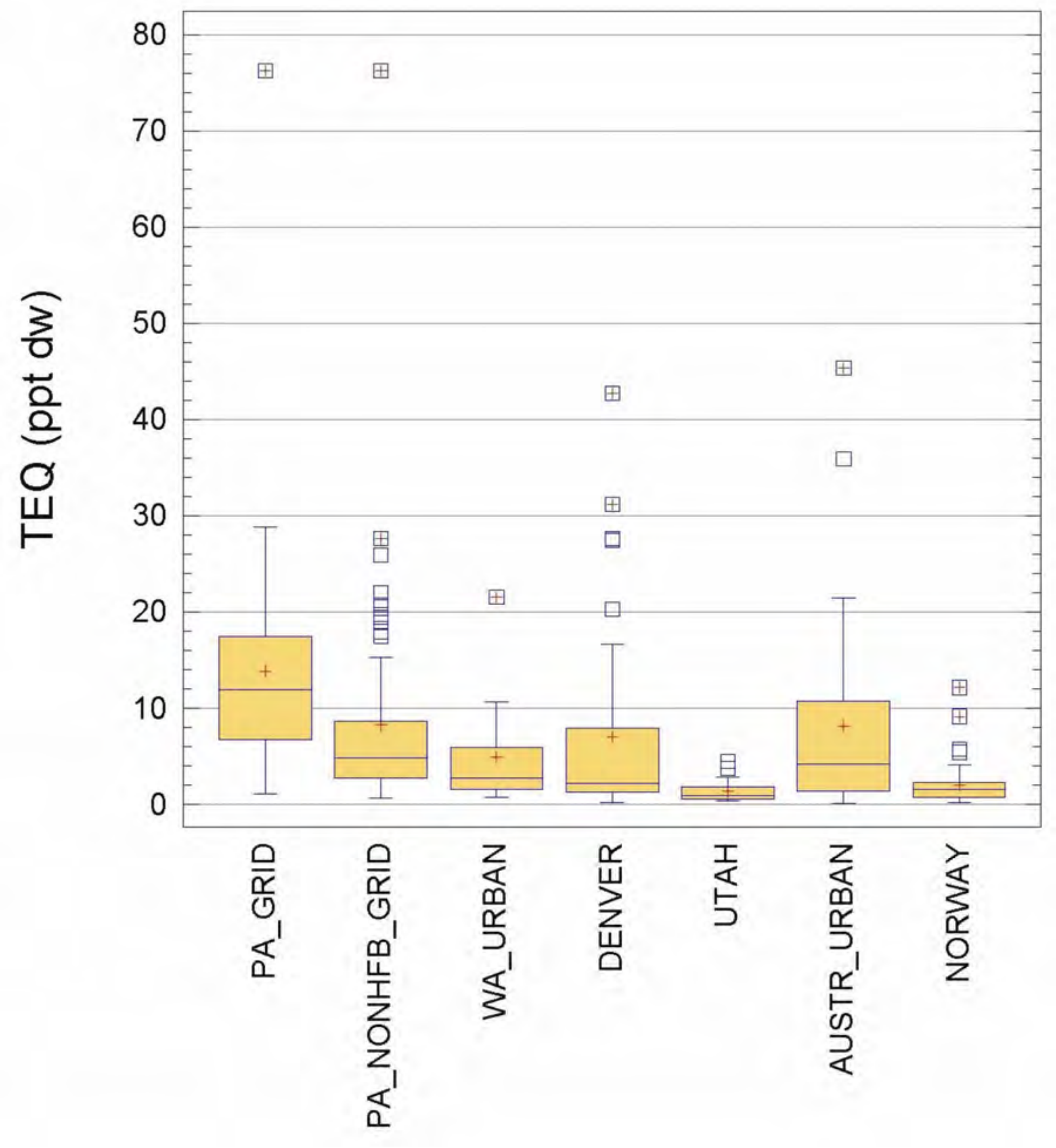


Figure 8-16 Comparison of soil TEQs: Port Angeles minus Source 3 versus urban soils

Note: For a description of Box-and-Whisker plots, refer to the text box included in Section 8.1.

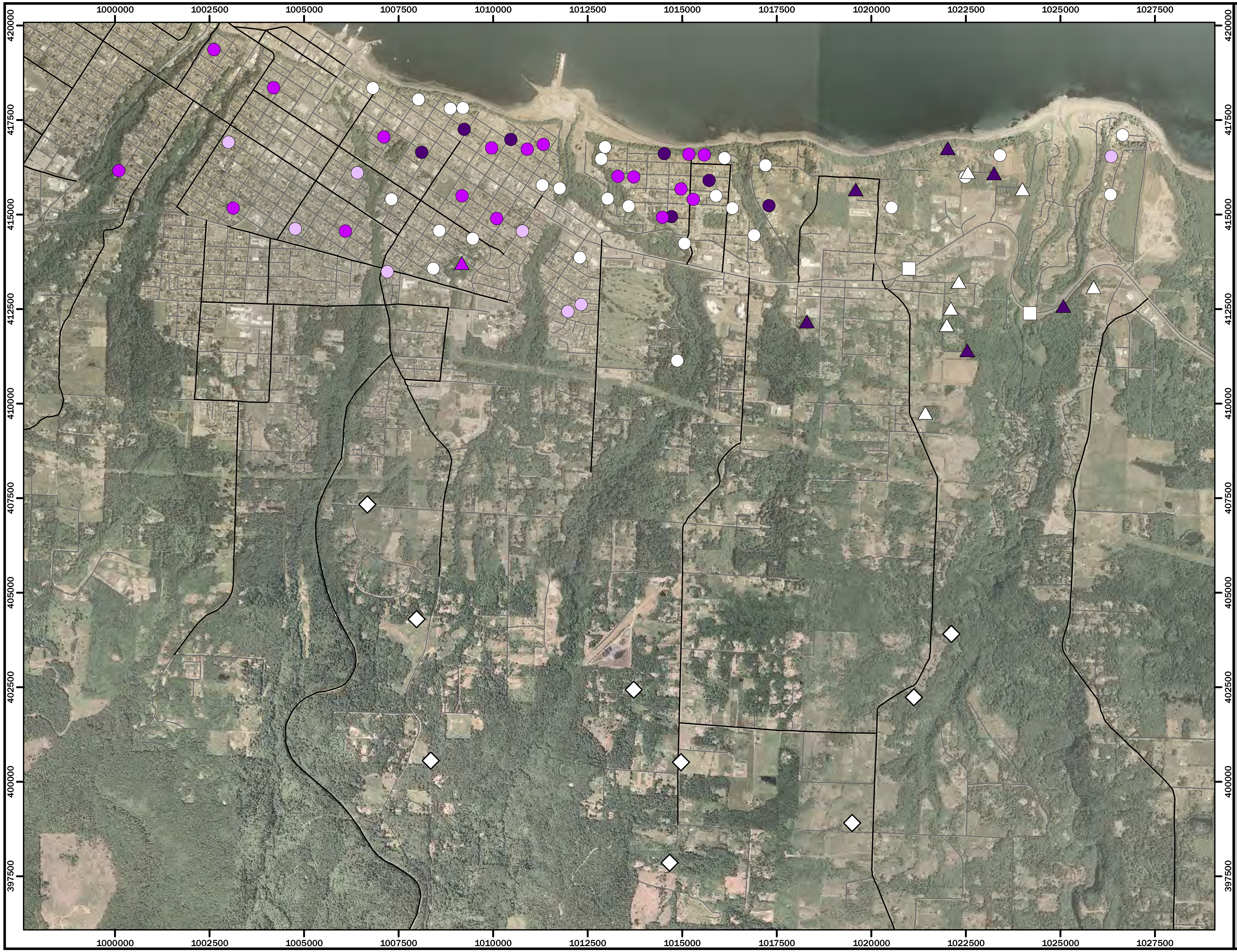


Figure 8-17.
Total TEQ Concentrations and Source 3 contributions
Rayonier Mill Off- Property
Soil Dioxin Study
Port Angeles, WA

Legend

Total TEQ and Source 3 Contributions

- ○ TEQ < 11, S3 (any)
- ● TEQ > 11, S3 < 4
- ● TEQ > 11, S3 > 4 and < 11
- ● TEQ > 11, S3 > 11

Soil sample type

- △ Forested
- ○ Grid
- □ Highway
- ◇ Transect

Arterial or Collector Road

Road

Notes:
1. Source 3 contributions to locations with total TEQs less than 11 ng TEQ/kg are not shown.
2. TEQ concentrations shown in ng/kg.

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0 1,250 2,500 5,000
feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (RDR)
Project:
K:\Projects\06-03386-006\Collected_Samples\TEQ_Calc\Combined Total TEQ - Source 3 TEQ - Overview.mxd

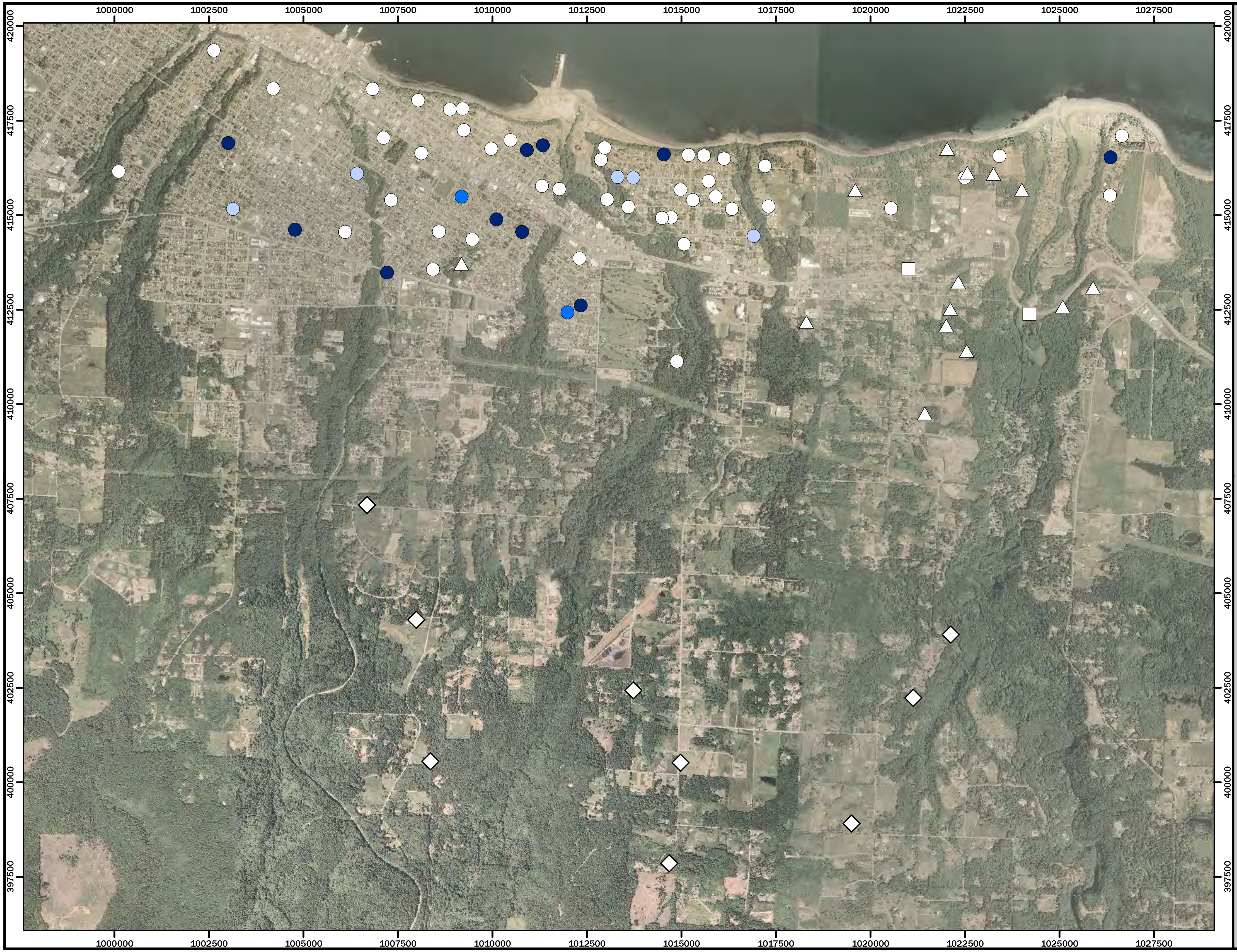

Figure 8-18. Unmixing model Souce 1 TEQ increments Rayonier Mill Off-Property Soil Dioxin Study Port Angeles, WA.

Legend

TEQ (ND = 1/2 DL) concentrations shown in ng/kg

○ 0 to 3

● 3 to 7

● 7 to 11

● > 11

Soil sample type

△ Forested

○ Grid

□ Highway

◇ Transect

Note: Contour plots used in these data evaluations cannot predict values at unsampled locations. Rather, they help visualize the large-scale distribution of the Port Angeles soils data. Local variability in dioxin/furan concentrations may be high and is likely to reflect individual property histories.

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0 1,250 2,500 5,000 feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (RDR)
Project:
K:\Projects\06-03386-006\Collected_Samples\TEQ_Calc\TEQ Increment Grid Dots and Contours.mxd

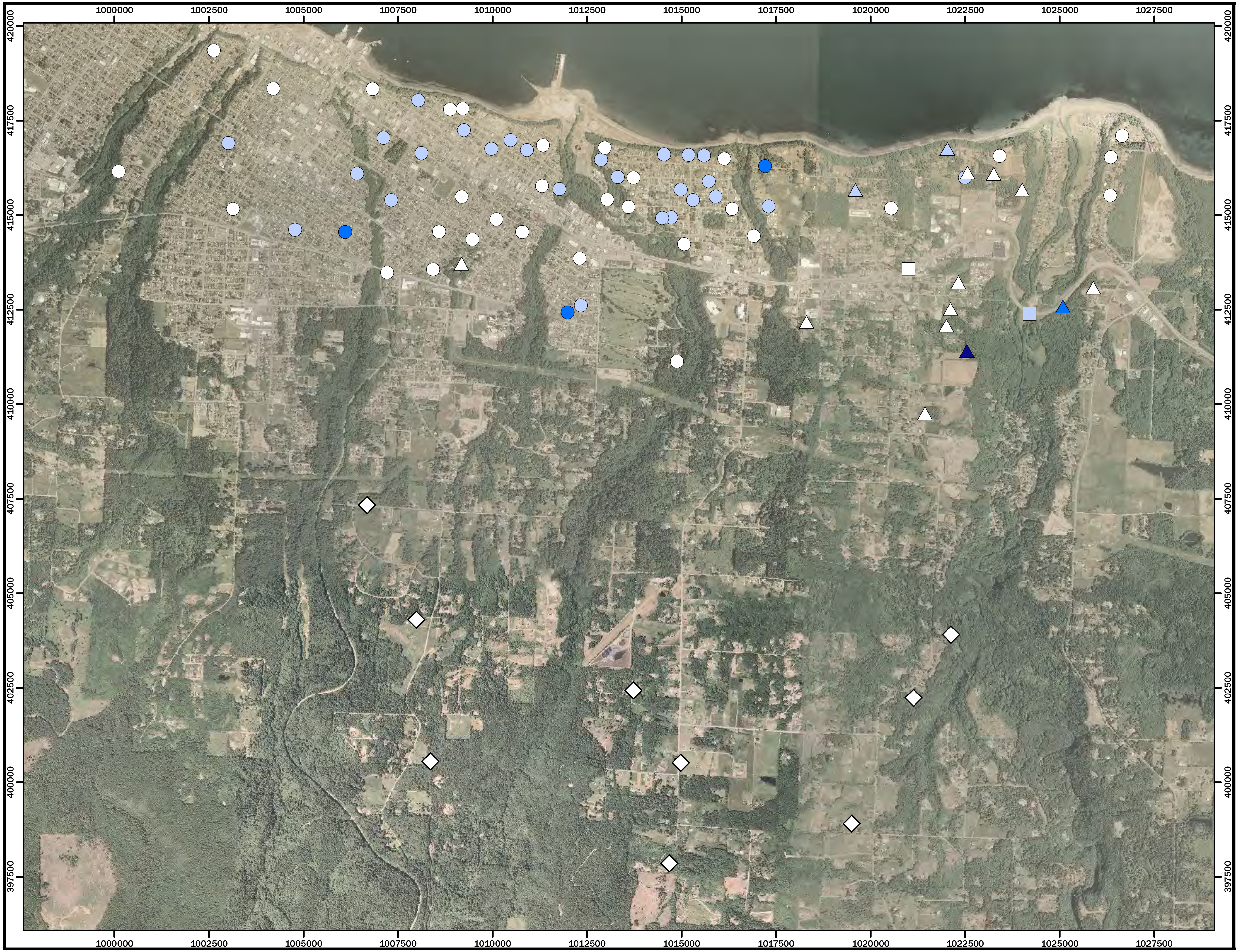

Figure 8-19.
Unmixing model Souce 2 TEQ increments
Rayonier Mill Off-Property Soil Dioxin Study
Port Angeles, WA

Legend

TEQ (ND = 1/2 DL) concentrations shown in ng/kg

- ○ 0 to 3
- ● 3 to 7
- ● 7 to 11
- ● > 11

Soil sample type

- △ Forested
- ○ Grid
- □ Highway
- ◇ Transect

Note: Contour plots used in these data evaluations cannot predict values at unsampled locations. Rather, they help visualize the large-scale distribution of the Port Angeles soils data. Local variability in dioxin/furan concentrations may be high and is likely to reflect individual property histories.

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HERRERA
ENVIRONMENTAL CONSULTANTS

0 1,250 2,500 5,000 feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (RDR)
Project:
K:\Projects\06-03386-006\Collected_Samples\TEQ_Calc\TEQ Increment Grid Dots and Contours.mxd

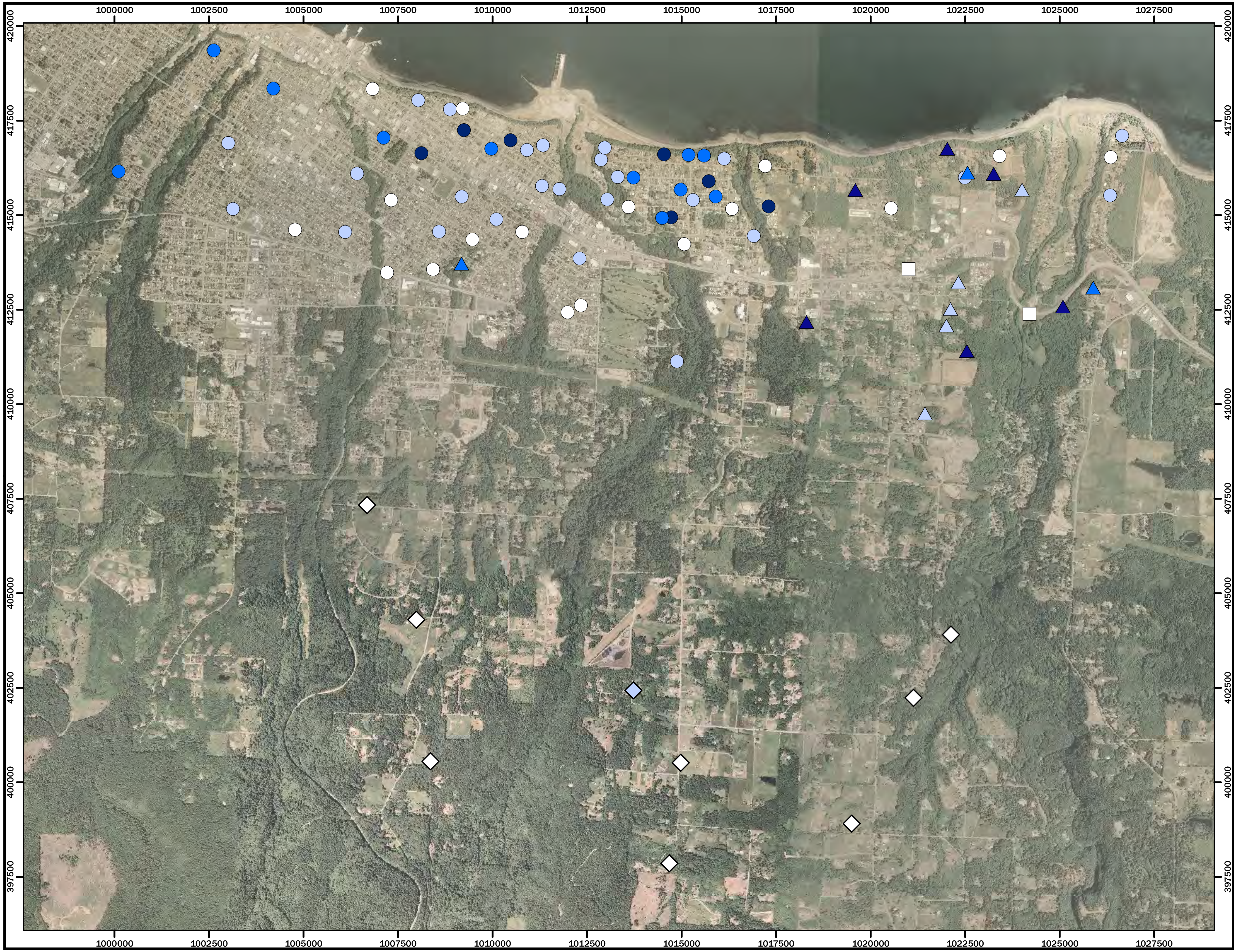

Figure 8-20.
Unmixing model Souce 3 TEQ increments
Rayonier Mill Off-Property
Soil Dioxin Study
Port Angeles, WA

Legend

TEQ (ND = 1/2 DL) concentrations shown in ng/kg

○	0 to 3
●	3 to 7
●	7 to 11
●	> 11

Soil sample type

△	Forested
○	Grid
□	Highway
◇	Transect

Note: Contour plots used in these data evaluations cannot predict values at unsampled locations. Rather, they help visualize the large-scale distribution of the Port Angeles soils data. Local variability in dioxin/furan concentrations may be high and is likely to reflect individual property histories.

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HERRERA
ENVIRONMENTAL CONSULTANTS

0 1,250 2,500 5,000
feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (RDR)
Project:
K:\Projects\06-03386-006\Collected_Samples\TEQ_Calc\TEQ Increment Grid Dots and Contours.mxd

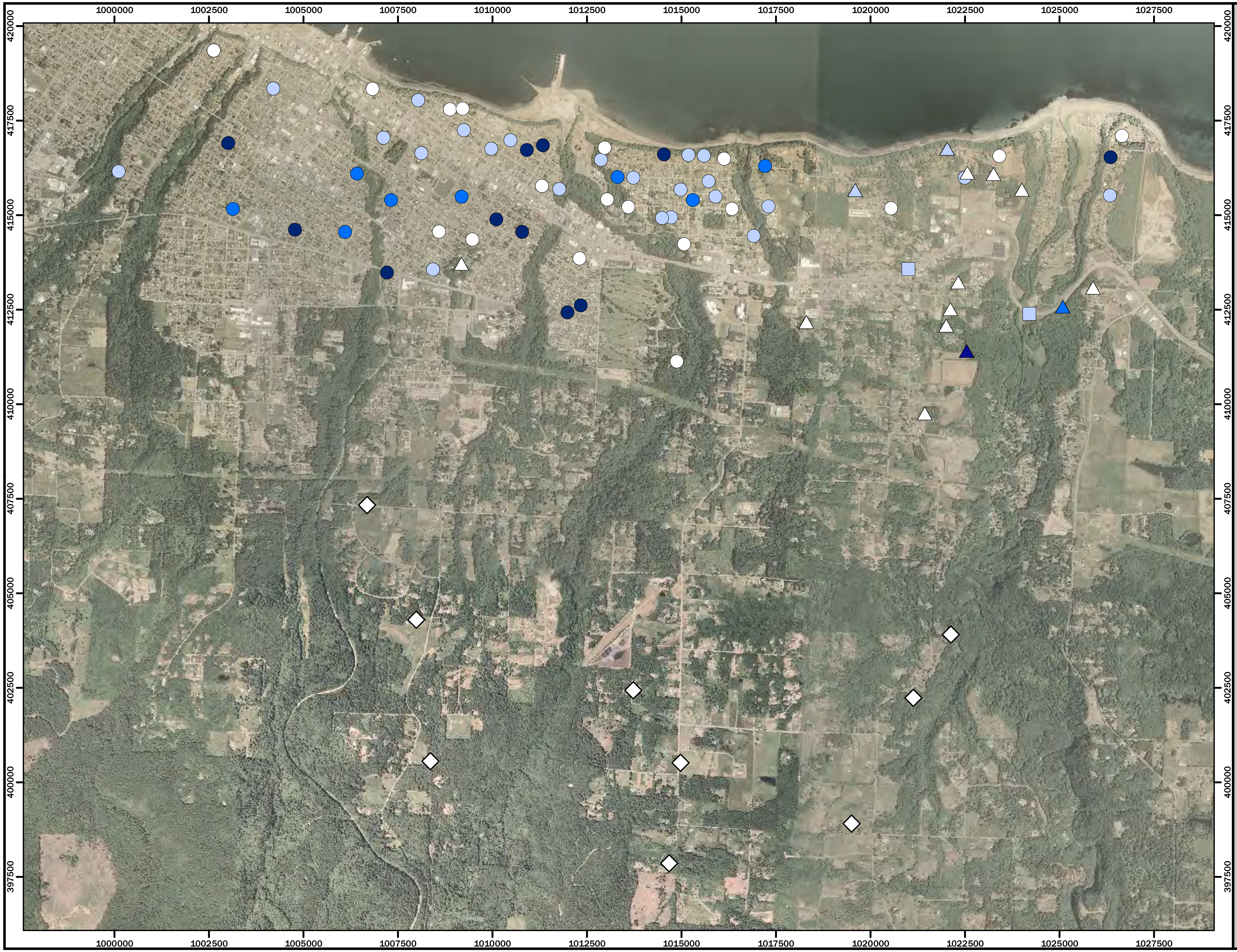

Figure 8-21.
Unmixing model Souce 1 plus Source 2 TEQ increments Rayonier Mill Off-Property Soil Dioxin Study Port Angeles, WA

Legend

TEQ (ND = 1/2 DL) concentrations shown in ng/kg

- ○ 0 to 3
- ● 3 to 7
- ● 7 to 11
- ● > 11

Soil sample type

- △ Forested
- ○ Grid
- □ Highway
- ◇ Transcent

Note: Contour plots used in these data evaluations cannot predict values at unsampled locations. Rather, they help visualize the large-scale distribution of the Port Angeles soils data. Local variability in dioxin/furan concentrations may be high and is likely to reflect individual property histories.

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HERRERA
ENVIRONMENTAL CONSULTANTS

0 1,250 2,500 5,000
feet

N

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

Produced By: GIS (RDR)
Project:
K:\Projects\06-03386-006\Collected_Samples\TEQ_Calc\TEQ Increment Grid Dots and Contours.mxd

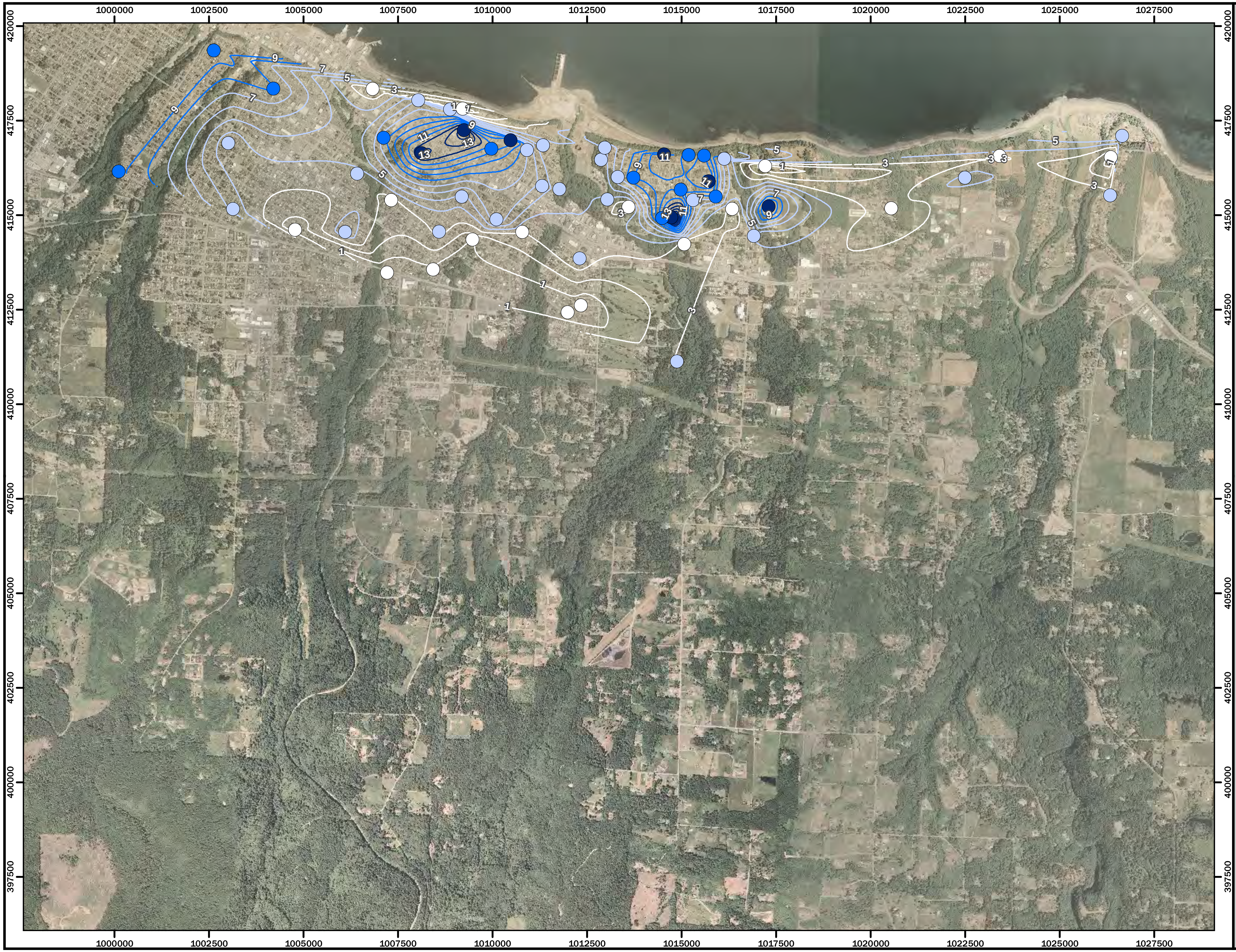

Figure 8-22.
Unmixing model Souce 3 TEQ increments: contour map - grid samples
Rayonier Mill Off-Property Soil Dioxin Study
Port Angeles, WA

Legend

TEQ (ND = 1/2 DL) concentrations shown in ng/kg

○	0 to 3
●	3 to 7
●	7 to 11
●	> 11

Soil sample type

△	Forested
○	Grid
□	Highway
◇	Transect

Note: Contour plots used in these data evaluations cannot predict values at unsampled locations. Rather, they help visualize the large-scale distribution of the Port Angeles soils data. Local variability in dioxin/furan concentrations may be high and is likely to reflect individual property histories.

ecology and environment, inc.
International Specialists in the Environment

HERRERA ENVIRONMENTAL CONSULTANTS

0 1,250 2,500 5,000
feet

Coordinates: Washington State Plane South
NAD 83 (feet)
Aerial: USDA, 2006

N

Produced By: GIS (RDR)
Project:
K:\Projects\06-03386-006\Collected_Samples\TEQ_Calc\TEQ Increment Grid Dots and Contours.mxd

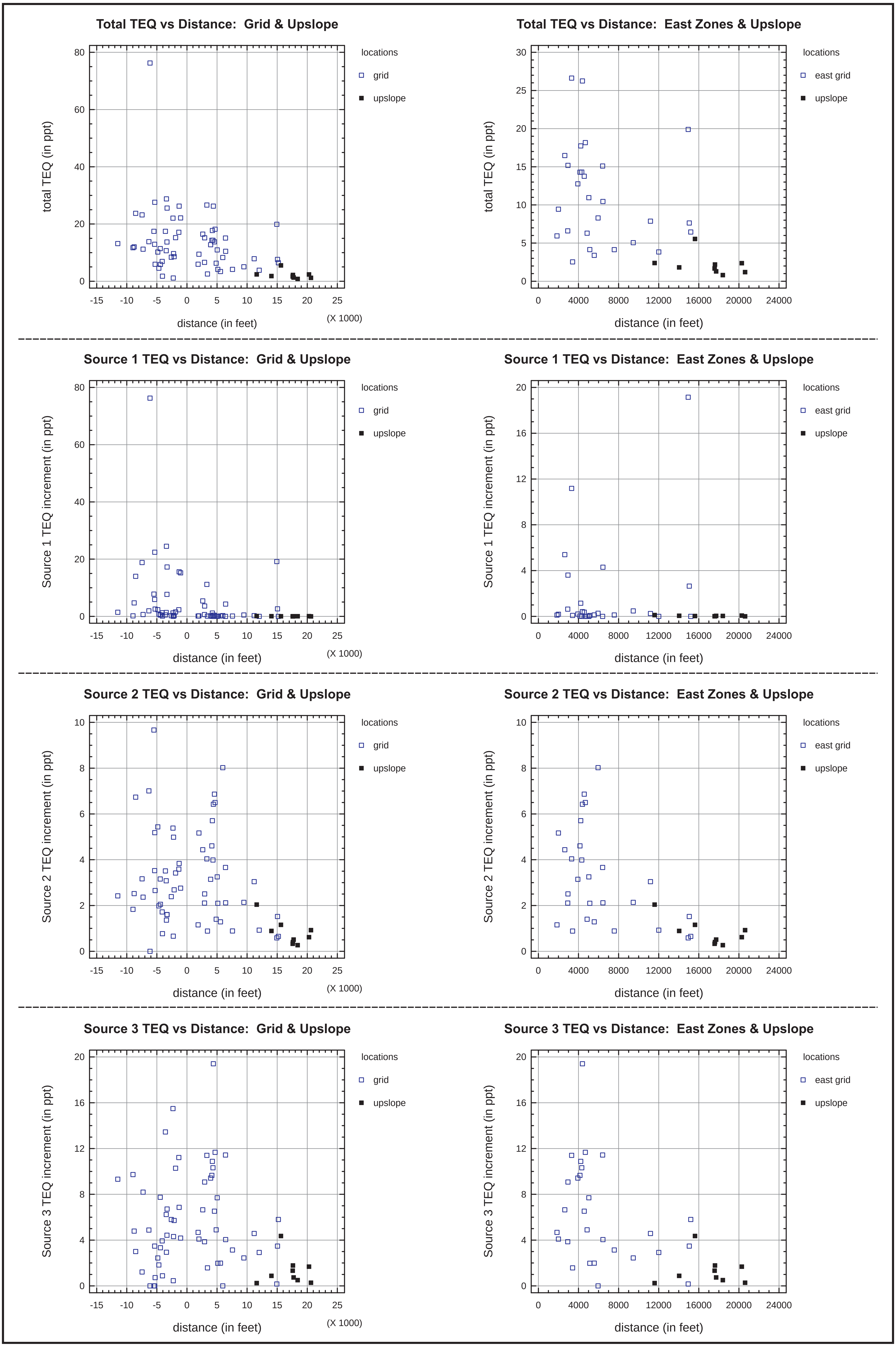

Figure 8-23 Scatter plots showing spatial trends for source increments

Note: Scatter plots in the left column include east and west sampling zones for grid samples [n=60], plus 9 upslope samples. Scatter plots in the right column include only east sampling zones for grid samples [n=28], plus 9 upslope samples. Axes in right hand column plots are rescaled to better show data patterns.

Appendices

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A CULTURAL RESOURCES MONITORING REPORT

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Rayonier Mill Off-Property Soil Dioxin Study

Cultural Resources Monitoring Report

Prepared for

Washington State Department of Ecology
Toxics Cleanup Program
300 Desmond Drive
Lacey WA 98504

Prepared by
Ecology & Environment, Inc.
720 Third Avenue, Suite 1700
Seattle WA 98104

Contract No. C0700036
Work Assignment No. EANE016

October 2010

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Table of Contents

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List of Tables

List of Figures

List of Acronyms and Abbreviations

DAHP	Department of Archaeology and Historic Preservation
E & E	Ecology and Environment, Inc.
Ecology	Washington Department of Ecology
EPA	U.S. Environmental Protection Agency
GOIA	Governor’s Office of Indian Affairs
LEKT	Lower Elwha Klallam Tribe
MTCA	Model Toxics Control Act
NHPA	National Historic Preservation Act
NPL	National Priorities List

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1.0 Management Summary

Ecology and Environment, Inc., (E & E) was contracted by the Washington Department of Ecology (Ecology) to conduct the Rayonier Mill Off-Property Soil Dioxin Study. This study involved collecting residential soil samples to test for dioxins and furans in the vicinity of the former Rayonier Mill. Composite surface soil samples were collected from 0 to 3 inches in depth.

Fieldwork for this project occurred from September 3 to 17, 2008, and from November 10 to 11, 2008. Cultural resources monitoring during the soil sampling effort resulted in recording three isolated artifacts and one historic road with a 1940s to 1950s abandoned Chrysler Corporation automobile. Locations of the artifacts and road are shown in Figure 1-1.

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2.0 Introduction

E & E conducted the Rayonier Mill Off-Property Soil Dioxin Study on behalf of Ecology, with fieldwork occurring from September 3 to 17, 2008, and from November 10 to 11, 2008. The effort involved collection of 89 surface soil samples throughout the greater Port Angeles, Washington, area. As part of this effort, cultural resources monitoring was provided by E & E archaeological staff.

Legal agreements between the Lower Elwha Klallam Tribe (LEKT), Rayonier, Inc., the U.S. Environmental Protection Agency (EPA), and Ecology establish requirements for subsurface investigational work to be monitored for cultural resources. Monitoring protocols were consistent with the LEKT Monitoring and Discovery Plan. Applicable legal agreements included:

- **Memorandum of Understanding between the LEKT and EPA regarding the Rayonier Port Angeles Paper Mill Site, 2/27/1998 –** This states that the EPA and the LEKT would assist each other in environmental investigations and keep each other informed, and that the LEKT would have opportunities to communicate interests and concerns.

- **Preliminary Agreement between the LEKT and Ecology, 3/19/1999 –** The parties agreed that the LEKT would support deferral of National Priorities List (NPL) listing if it received satisfactory assurance of sufficient resources for substantive tribal participation and oversight. The conditions state that a professional archaeologist approved by the LEKT would monitor disturbances of native soils and have stop work authority. Also, the site boundaries would include the area of influence of chemical contamination caused by activities at the former Rayonier Mill. Ecology would seek the LEKT's concurrence at all major decision points in the cleanup process.

- **Cooperative Agreement between the LEKT and Rayonier, Inc., on the investigation and cleanup of the Rayonier Port Angeles Mill Facility, 6/21/1999 –** Rayonier, Inc., would reimburse the LEKT for the costs of activities related to the investigation and cleanup of the site up to $250,000 per year; Rayonier would allow the LEKT site access; Rayonier would have a representative of Larson and Associates available for all sampling or cleanup activities on its property and would comply with that firm's decisions about treatment of any cultural resources found.

- **Deferral Agreement on the Rayonier Mill Site, between EPA, Ecology, and LEKT –** All three agreements listed above are attached to this deferral agreement. The deferral agreement describes action Ecology would take to ensure adequate response action required to defer NPL listing activities by EPA. The agreement stipulates Ecology's responsibility to provide timely cleanup under the Model Toxics Control Act (MTCA), to consult with the Tribe, and to support the public's right of participation. It defines EPA's role as generally limited to reviewing state annual reports and consulting on proposed remedies.

- **Tse-whit-zen Village Settlement, City of Port Angeles, Port of Port Angeles, and LEKT –** The settlement pertains to the graving dock area. This settlement (1) amicably resolved the issues at the historic Tse-whit-zen Village site; (2) ensured the site, the remains, and artifacts were protected; (3) replaced and enhanced the economic stimulus that would have been generated by the graving dock project; (4) created a process for avoiding possible future land-use conflicts; (5) allowed development to continue while providing appropriate protection of archaeological sites; (6) promoted cultural awareness; and (7) ended the pending litigation. The statement states that the City would hire an archaeologist for a five-year period to analyze and map archaeological resources on the Port Angles waterfront. The statement also declares Washington State's responsibility to reimburse the City for the costs of employing the archaeologist and sets protocol to ensure clear communication when archaeological resources are discovered.

- **Executive Order 05-05 –** This order requires all capital construction projects and land acquisitions for the purpose of a capital construction project to undergo review with the Department of Archaeology and Historic Preservation (DAHP), and requires affected tribes to determine potential impacts to cultural resources. It states that DAHP and the Governor's Office of Indian Affairs (GOIA) should be notified and invited to any meeting with affected tribes during which matters concerning cultural resources related to a capital construction project will be discussed.

3.0 Setting

3.1 Natural Setting

The city of Port Angeles is located in Clallam County, Washington, along the northern coast of the Olympic Peninsula. It sits on a natural harbor, which Spanish explorers named Puerto de Nuestra Señora de Los Angeles (Oldham 2007). The surrounding topography gently slopes from the foothills of the Olympic National Park to Port Angeles Harbor, which opens on the Strait of Juan de Fuca. A long sand spit, Ediz Hook, juts into the Strait of Juan de Fuca. Elevations of 400 to 500 feet are found at the southeastern border of the city. Peabody, Tumwater, Ennis, and Valley creeks cut through the city and empty into Port Angeles Harbor.

Geology and Geomorphology

The retreat of the glaciers at the end of the Pleistocene is largely responsible for creating the current morphology of the Puget Sound Basin (Shipman 1989), which includes the Port Angeles area. A mile-thick glacier covered Washington until around 14,000 BC, when the glacier began to melt rapidly. While the melting of the glaciers caused sea levels to rise, the release of the glacier's weight from the earth's crust caused the crust to rebound and rise. By approximately 6,500 years ago the northern part of Washington, including the study area, had completed the bulk of the rebounding (Stilson et al. 2003). Evidence suggests that in the late Pleistocene (around 10,700 BP) the sea level was approximately 60 meters lower than present levels (Mosher and Hewitt 2004). Port Angeles Harbor was formed approximately 5,000 years ago when Ediz Hook began to form (Wessen 2007).

The rising sea level is thought to have inundated many of the early human settlements that would have been associated with older beach lines. These sites were probably villages, which typically are found 5 to 20 feet above the high water mark and near the mouths of rivers and other areas to provide a diverse range of resources. Resource procurement sites may well have been on landforms of higher elevation (Stilson et al. 2003). To date, there are no known village or habitation sites in northern Washington that date to older than 4,300 BP (Stilson et al. 2003). It is thought that there could be well-preserved archaeological sites currently underwater in many areas of the Washington coast.

Climate

The average annual precipitation for Clallam County is consistently less than 30 inches (Western Regional Climate Center 2007). Average maximum temperatures range from 65°F to 70°F during the summer months, rarely exceeding 90°F, and from 45° to 50°F during the winter months, rarely dropping below 30°F (Western Regional Climate Center 2007).

Fauna

Marine resources include harbor seals (*Phoca vitulina),* sea otters (*Enhydra lutris*), and shellfish, such as littleneck clams (*Protothaca staminea*), butter clams (*Saxidomus giganteus*), horse clams (*Tresus sp.),* heart cockles (*Clinicardium nuttallii*) and bent nose clams (*Macoma nasuta*). Salmon was a primary resource for the Port Angeles area (Wilt and Roulette 2001).

Flora

The project area is within the *Tsuga heterophylla* Zone of Western Washington. This zone is characterized by extensive stands of conifer forest including Douglas fir *(Pseudotsuga menziesii)*, Western hemlock *(Tsuga heterophylla)*, grand fir *(Abies grandis)*, western red cedar (*Thuja plicata)*, red alder *(Almus rubra)*, bigleaf maple *(Acer macrophyllum)*, and Pacific madrone *(Arbutus menziesii)*. Plants found within the project area include Western blackcurrant (*Ribes petiolare*), golden currant (*Ibes aureum*), Western chokecherry (*Prunus virginiana demissa*), squaw potato (*Perideridia oregana*), Indian potato (*Orogenia linearifolia*), and creeping juniper (*Juniperus horizontalis*). Indigenous populations likely used all of these edible plants to supplement the wide variety of saltwater, terrestrial, and freshwater resources in the Port Angeles Harbor vicinity (Wilt and Roulette 2001).

3.2 Cultural Setting

Prehistory

The earliest archaeological sites recorded in the northern Puget Sound Lowland date to approximately 4,500 years BP. The cause of this relatively recent record is thought to be lower sea levels in the terminal Pleistocene and early Holocene (Shipman 1989).

In later prehistory, groups in the northwest were expert hunter-gatherers who lived in permanent village sites. Although wild resources formed the base of their subsistence, the groups had individuals who specialized in many crafts such as hunting, fishing, and tool-making. By 1,000 BP, settlements of several hundred people could be found. Plentiful large cedar trees were used for building houses and dug-out canoes. Canoes were used for distance travel for resource exploitation and also maintaining long distance social networks (Fagan 2000).

Ethnography and Ethnohistory

The traditional territory of the Klallam stretched along the south shoreline of the Strait of Juan de Fuca, from the Hoko River east to Discovery Bay (Gunther 1927). Generally, the Klallam lived in small villages located in sheltered coves, protected from the sea by a sand spit and having a sufficiently wide beach for outdoor activities (Gunther 1927). Winter villages consisted of one to five or six cedar plank houses. Villages on coastlines had houses arranged facing the water. Temporary shelters were constructed of mats of woven rushes and resembled the permanent plank house (Gunther 1927). These shelters were used for resource-gathering campsites.

The Klallam often traveled to areas of seasonal resource gathering and established temporary campsites for collection and processing. Gunther (1927) also observed that when an extended stay in the resource area was expected, cedar planks were transported and used to reinforce the mat structures. People boiled water and cooked food in watertight wooden boxes or baskets by heating rocks and dropping them into the water.

According to Gunther (1927), Klallam people hunted whales, porpoises, blackfish, and seals. Seal hunting was the most economically viable practice and when a seal was caught it was shared by the entire village. The taking of whales was opportunistic. Unlike the nearby Makah, the Klallam did not set out on whale hunts but rather waited until a whale was sighted near their village before pursuing it (Gunther 1927). Only men from wealthy families could be involved in the taking of whales; it was a hereditary right. Waterfowl such as ducks were ensnared using nets strung between high poles to catch them in flight. These nets were set up on sand pits or marshes in the early morning or at dusk. Ducks were also trapped at night from canoes with a net affixed to a long cedar pole. From the canoe, the hunter could easily bring the net down over swimming ducks. Geese and swans were trapped in the same manner (Gunther 1927). Elk and deer were hunted with bow and arrow throughout the Olympic Peninsula. Gunther (1927) states that the Klallam had no traditional, tribal, or familial hunting grounds but the whole Olympic Range was available to everyone. Land mammals such as deer, bear, and elk were more often hunted if they wandered onto the beach. An animal sighted on the beach was at times chased into the water. Hunters would follow the animal in a canoe until it was exhausted (Gunther 1927). One source states that the peoples of the Northwest Coast made blankets using dog wool (Waterman 1924).

The locations of burial sites varied over time and among groups. In some parts of western Washington, small off-shore islands or wooded slopes close to villages were cemetery areas. Isolated burials are found in a variety of locations. Winter villages usually had an associated cemetery, which was at the end of a sand spit or in wooded areas (Gunther 1927). Burials were either laid directly on the sand or supported on scaffoldings two to three feet high. The body was often covered by a small shed or placed in a canoe. (Gunther 1927). According to ethnographic sources (Gunther 1927), cemeteries on sand spits were well away from areas used for habitation or for resource processing activities. Shortly after Euroamerican contact, entire villages were decimated by disease and thus became cemeteries (Stilson et al. 2003). Most of a man’s belongings were given away at death (Eells 1887).

For ceremonial purposes, the Klallam used ochre. Iron-oxide, or yellow ochre, turns red when heated. According to Gunther (1927), the ochre is “burnt in the fire” and spread with the fingers to the skin on a base of deer tallow. The best ochre was obtained from Hood Canal and the Klallam traveled there to collect it. The ochre was carried in small deerskin bags and was sometimes traded with the Makah or Vancouver Island people (Gunther 1927).

History

The first European contact with the Klallam was in July 1788 by Robert Duffin, an Englishman who had been sent on a longboat expedition from the west coast of Vancouver Island. Maritime exploration brought the Spanish to Klallam Territory in 1790, when Manuel Quimper anchored his boat in Freshwater Bay near the Elwha River. The first exploration of the Olympic Peninsula was conducted by George Vancouver in 1792. These early explorers brought diseases to the indigenous people. The tribes had no immunity against sicknesses such as smallpox, measles, influenza, and tuberculosis. Whole villages were decimated (Lower Elwha Klallam Tribe 2008; Oldham 2007; University of Idaho 2008).

European occupation of the Port Angeles area began in earnest in the 1860s as homesteaders arrived, displacing many Klallam people. The Indian Reorganization Act of 1934 helped the Klallam Tribe obtain 327 acres of land, which officially became the Elwha Klallam Reservation in 1968 when the Tribe became federally recognized. In 1974 the Tribe regained its fishing rights from the state of Washington and built a fish hatchery (Lower Elwha Klallam Tribe 2008).

In 1859, the Cherbourg Land Company formed to plat a townsite and sell lots. The U.S. Army Corps of Engineers platted a federal townsite on land designated as a federal reserve by President

Abraham Lincoln. In 1861, the first trading post was established and the Ediz Hook lighthouse opened in 1865 (Oldham 2007).

The Puget Sound Co-operative Colony revitalized the community after several years of declining interest. The Colony set up along the west side of Ennis Creek. By 1890, the townsite had 3,000 residents (Oldham 2007).

3.3 Regulatory Setting

Regulations, orders, and agreements specific to the former Rayonier Mill and the City of Port Angeles are described in Section 2. General state and federal regulations pertaining to cultural and historic resources are described below.

State Regulations and Standards

In Washington state several laws and statutes protect archaeological sites and Native American graves. These include:

- *The Indian Graves and Records Act [RCW 27.44]* – Protects Native American burials, petroglyphs, and pictographs from intentional disturbance.
- *The Archaeological Sites and Resources Act [RCW 27.53]* – States that a permit is required before knowingly disturbing any historic or prehistoric archaeological resource or site on private or public land.
- *Abandoned and Historic Cemeteries and Historic Graves [RCW 68.60.040 and RCW 68.60.050]* – Establishes protection for historic cemeteries and graves. Persons inadvertently disturbing historic graves, including disturbance through construction, must reinter the remains under the supervision of the DAHP.
- The Advisory Council on Historic Preservation also has pertinent guidelines such as an *Archaeological Excavation and Removal Permit [WAC 25-48]*.

Washington Governor Chris Gregoire signed Executive Order 05-05 into action in November 2005. This Order requires state agencies with capital improvement projects to integrate the DAHP, the GOIA, and concerned tribes into their capital project planning process. The purpose of this action is to ensure that state agencies take actions to avoid or mitigate any adverse effects their undertaking may have on cultural resources, and to ensure that the Native American community has a chance to express its concerns with projects that could adversely affect tribal interests. Executive Order 05-05 also mandates that state agency employees managing such projects undergo government-provided training pertaining to the importance and treatment of cultural resources.

Federal Regulations

Cultural resources are protected by the National Historic Preservation Act (NHPA) of 1966, the Archaeological and Historic Preservation Act of 1974, the Archaeological Resources Protection Act of 1979, and the regulations (36 CFR 800) that implement Section 106 of the NHPA. Section

106 requires federal agencies to consider the impacts of their actions on properties listed, or eligible for listing, in the National Register of Historic Places.

Other laws and guidelines that protect cultural resources include:

- *Executive Order 11593* – Protection and Enhancement of Cultural Environment (16 U.S.C. 470 [Supp. 1, 1971]).
- *Native American Graves Protection and Repatriation Act* (PL 101 – 601; U.S.C. 3001 – 3013).
- *Determination of Eligibility for Inclusion in the National Register* (36 CFR 63).
- *Recovery of Scientific, Prehistoric, and Archaeological Data* (36 CFR 66).
- *Curation of Federally Owned and Federally Administered Archaeological Collections* (36 CFR 79).
- *Department of Defense Directive 4710.1* – outlines the policy to incorporate historic preservation requirements into all Defense Department activities.

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4.0 Investigation Design

The Cultural Resource Monitoring Protocol is provided in the *Rayonier Mill Off-Property Soil Dioxins Study Sampling and Quality Assurance Plan* (E & E 2008). The protocol is consistent with standard cultural resources monitoring practices and the LEKT Monitoring and Discovery Plan, which the LEKT provided to E & E. Cultural resources monitoring procedures were approved during meetings between E & E archaeologist Sandra Pentney, LEKT archaeologist Bill White, and City of Port Angeles archaeologist Derek Beery on May 1, 2008.

In preparation for this project, a cultural resources records search was conducted at the DAHP to identify previously recorded resources in the area. The data recovered during this search were used to plan the sampling procedures to avoid known cultural resources. The study design is biased toward choosing locations that are the least disturbed so that samples will reflect the contaminant deposition that actually occurred. This approach increases the chances that cultural resources could be encountered.

Cultural resources monitoring involves the presence of a qualified archaeologist when soil samples are collected, to protect cultural resources from disturbance. The sampling procedure states that the sampling team would collect subsamples from the four corners and the center of a 10-foot-by-10-foot template. This method was subject to field modification as conditions required. Prior to sampling, the existing ground cover was removed to expose the soil layer, and a stainless steel spade or trowel was used to collect the sample. Following sampling, the hole was filled with topsoil and the ground cover was replaced. The sample was hand-kneaded to remove roots and any debris larger than two centimeters. Rocks and other debris were avoided as much as possible during sample collection.

The sampling was conducted by two crews. An archaeologist was present at all times with each crew. The archaeologist had stop work authority if any cultural resources were encountered during the sampling. All sample locations were examined prior to any ground cover removal and the cleared surface was examined prior to sampling. The archaeologist completed a Sample Documentation Form and took photographs for each sample location.

When artifacts were found, the find was documented and properly recorded on Washington state cultural resources forms, and the artifact was returned to the hole from which it was recovered and covered over with topsoil. The LEKT archaeologist, City of Port Angeles archaeologist, and land owner were notified of the find. The land owner, LEKT, City of Port Angeles, and Ecology were provided with copies of all of the documentation associated with the find, including the isolate record form required by the DAHP.

The project protocol required E & E to notify the LEKT and the City of Port Angeles archaeologist 24 hours before beginning sampling activities that required archaeological monitoring. An E & E archaeologist was to examine all soil samples collected during the project. Cultural materials that could be encountered include, fire modified rock, animal bone, lithic debitage (sharp rock waste from making stone tools), flaked or ground stone tools, cordage and fibers, charcoal, ash, exotic rocks and minerals, historic bottles, ceramic shards, nails, wire, and wood. All finds were to be extensively documented using photographs, sketches, scaled drawings, and written descriptions.

If an artifact was discovered, the LEKT, City of Port Angeles, and Ecology were to be notified as soon as feasible. The points of contact included:

LEKT
- Primary Contact: Bill White, Tribal Archaeologist, (360) 460-1617
- Secondary Contact: Larry Dunn, Tribal Cleanup Project Manager, (360) 452-8471 x126

City of Port Angeles
- Primary Contact: Derek Beery, City of Port Angeles Archaeologist, (360) 417-4704
- Secondary Contact: Nathan West, Deputy Director of Community and Economic Development, (360) 417-4751

State
- Dr. Rob Whitlam of DAHP (360-586-3080)

If human remains were encountered in any of the samples, the E & E archaeologist was to immediately notify the Port Angeles City Police, the City of Port Angeles archaeologist, and the Clallam County coroner. The LEKT and the DAHP also were to be notified if it were determined that the remains were of Native American origin. Documentation (photographs) of human remains were not to be collected until approval was issued by the City of Port Angeles archaeologist and/or the LEKT. Contact information for the police and the coroner was provided:

- Port Angeles Police Department (non-emergency): (360) 452-4545

Clallam County Coroner: Deborah Kelly (360) 417-2297

It was determined after the dates of the first sample gathering that further samples were required to complete the study. E & E crews collected samples for two extra days, November 10 and 11, 2008. These samples were monitored by two local archaeologists. City archaeologist Derek Beery provided monitoring services on November 10, and LEKT tribal archaeologist Bill White provided monitoring services on November 11. Both archaeologists followed all of the previously established protocols. The results of these sampling activities are also included in this report.

5.0 Field Monitoring Methods

During the field sampling, each sample site was visually inspected by the archaeologist to ensure there were no surface signs of cultural resources. If there were no signs, the archaeologist dug five holes in a confined area. The holes were oriented either in a 10-foot-by-10-foot square pattern, or in a linear pattern with 10 feet between the holes, depending on the characteristics of the sample collection location.

The on-site archaeologist dug holes approximately 10 inches square and approximately 4 inches deep using a shovel. The soil removed was examined to ensure that cultural resources were not present.

Soil samples were collected from the side walls of each hole using sterile spoons. The samples were placed in sterile bowls to be homogenized prior to being placed in the sample jars. Both the sample collection and the homogenization activities were monitored by the on-site archaeologist to ensure that artifacts were not inadvertently collected with the spoon. Photographs were taken and field recording forms were completed for each sample location.

When a cultural resource was discovered, DAHP isolate and/or site recordation forms were completed, the find photographed, and the artifacts reburied on-site. These forms have been submitted to the DAHP for archiving, and copies of the forms have been given to the landowners.

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6.0 Report of Findings

A literature review was conducted at the DAHP on April 30, 2008. Forty previously recorded investigations have been conducted in the greater Port Angeles area. A summary of previous work is presented in Table 6-1.

During the soil sampling effort in September 2008, four of the 85 sample locations contained cultural resources (Table 6-2). Locations are shown in Figure 1-1. Isolate records are provided in Appendix A, but property owner names and addresses have been redacted from the forms. All of the resources discovered during the project represent the historic era of Port Angeles. The discovered resources include fragments of historic stone wear and ceramics (Figure 6-1), a piece of terra cotta tile (Figure 6-2), a piece of red brick (Figure 6-3), and an overgrown, historic road (Figure 6-4) with an abandoned 1940s to 1950s model Chrysler Corporation automobile (Figure 6-5).

The soil sampling efforts that occurred on November 10 and 11, 2008, did not yield any cultural resources findings.

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7.0 Discussion and Interpretation

While four sample locations yielded historic artifacts, these resources may not yield information pertinent to interpreting the past of the Port Angeles area. Maker's marks or patterns on brick and household items are usually used to identify the approximate age of an artifact or relative date of the site. There were no maker's marks or distinguishing patterns available on any of the construction or houseware artifacts that were recorded.

The historic road at sample location T103SS is not recorded on historic maps at the Port Angeles Library, nor on any of the historic maps found online. On a 1955 road map of the area, the location is shown to be owned by Grace E. Melick, but there is no road on the map that corresponds with the location of the road in question (Figure 7-1).

The abandoned automobile on the historic road is likely a 1940s to 1950s model Chrysler Corporation automobile. There is no way to establish when the car was abandoned at its current location.

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8.0 Management Considerations

While the cultural resources monitoring did result in recording four cultural finds, the finds offered little information on the history of the area. These resources are not likely to be considered findings of significance.

Since the soil sampling effort is complete and no further sampling at the same locations is needed, no further cultural resources monitoring work is required on this project.

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Tables

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Table 6-1 Results of Records Search conducted at the DAHP

NADB Number	Author	Date	Title
1332732	Randolph, Joseph	1987	Summary of Cultural Resource Management Activities for the Spokane District, BLM Fiscal Year 1986
1332741	Randolph, Joseph	1987	Halleur Intrusion
1333257	Bergland, Eric O.	1983	Prehistory and Ethnography of Olympic National Park
1333521	Shipman, Hugh	1989	Vertical Land Movements in Coastal Washington: Implications for Relative Sea Level Changes
1334584	Robinson, Joan M.	1995	A Cultural Resources Survey of the Washington State Department of Transportation’s SR 101: Lees Creek Fish Passage Project
1334591	Solimano, Paul S.	1995	Letter to Gary Kentworthy Regarding Port Angeles Waterfront Trail Phase V
1339717	Greengo, Robert	1983	Prehistoric Places on the Southern Northwest Coast
1340419	Forsman, Leonrad, A.	2001	Letter to Jack Anderson Regarding Earthen SSL Berm Removal Archaeological Monitoring
1341199	Rooke, Lara C.	2002	Letter Report: Procedures and Results of a Cultural Resources Survey of Cingular Wireless Tower Site WA-718 (Shane Park) in Clallam County, Washington
1342395	Trudel, Stephanie, E.	2003	Letter to Jack Anderson regarding Archaeological Monitoring for Geotechnical Boring and Soil Sampling
1342893	Weaver, Dean	2004	Cultural Resources Assessment for the William R. Fairchild International Airport Land Transfer
1343558	Dellert, Jenny	2004	Archaeological Resources and Traditional Cultural Places Assessment, Crown Park Storm and Sanitary Sewer Project
1343696	Lewarch, Dennis E.	2004	Final – WSDOT Port Angeles Graving Dock Facility Treatment and Monitoring Plans for the Tse-whit-zen Site (45CA523) and Shotwell Recycling Property Recovery, Port Angeles
1343722	Cooper, Jason B.	2004	Cultural Resources Study of the Proposed Clallam County Draper Road Improvement Project
1343781	Lewarch, Dennis E.	2003	Port Angeles Graving Dock Facility Project Distribution of Archaeological Deposits at 45CA523 Identified during Archaeological Site Assessment
1343793	Forsman, Leonard A.	2002	Letter to Jack Anderson regarding Final Port Angeles Mill-Finishing Room/Ennis Creek Excavation and Waterfront Trail Bridge Abutment Excavation Archaeological Monitoring
1343828	Kramer, Stephanie	2000	Letter to Jack Anderson regarding Archaeological Monitoring of the Stormwater Conveyance Project at the Rayonier Port Angeles Mill
1343843	Forsman, Leonard A.	1999	Letter to Jack Anderson regarding Cultural Resource Monitoring for the Water Pipeline Reroute Trench at the Rayonier Port Angeles Mill

Table 6-1 Results of Records Search conducted at the DAHP

NADB Number	Author	Date	Title
1343891	Robbins, Jeffrey R.	1998	Letter to Paul Perlwitz regarding Cultural Resource Assessment of the Water Filter Plant and the South Property, Rayonier Incorporated, Port Angeles Mill
1343892	Robbins, Jeffrey R.	1998	Letter to Paul Perlwitz regarding Report for Cultural Resource Monitoring of EPA Geotechnical Testing at the Rayonier Port Angeles Mill
1343893	Robbins, Jeffrey R.	1998	Letter to Jack Anderson regarding Cultural Resource Monitoring of Excavations at the Finishing Room, Rayonier Port Angeles Mill
1343894	Robbins, Jeffrey R.	1998	Letter to Gary Kentworthy regarding Cultural Resource Monitoring for Construction Excavation of the Peabody
1343900	Robbins, Jeffrey R.	1998	A Cultural Resources Survey of Washington State Department of Transportation’s SR 101: Golf Course Road to Myrtle Street Project
1344070	Robbins, Jeffrey R.	1997	Letter to Paul Perlwitz regarding Cultural Resource Assessment in Association with the Dismantling and Remediation Project for the Rayonier, Incorporated, Port Angeles Mill
1344076	Robbins, Jeffrey R.	1998	Letter to Bruce Beane regarding Cultural Resource Monitoring of the Raw Water Pipeline Leak Investigation, Diashowa America Port Angeles Mill
1344093	Robbins, Jeffrey R.	1997	Rayonier, Incorporated Port Angeles Mill, Dismantling and Remediation Project Cultural Resource Assessment
1344112	Holstine, Craig	1995	Letter to Ken Stone regarding SR 101: SR 112 to Doyle Street, MP 242.58 to 246.22, XL-0392
1344237	None Stated	2004	Port Angeles 8th Street Bridge Replacements
1345086	Larson, Lynn L.	2005	Letter to Steve Sperr regarding Revised Crown Park Storm and Sanitary Sewer Project Archaeological Resources Monitoring.
1346904	Lewarch, Dennis E.	2005	Fieldwork Status Report, Data Recovery Excavation and Archaeological Construction Monitoring at the TSE-WHIT-ZEN Site (45CA523)
1348626	Holstein, Craig	1997	Letter to Ken Stone RE: SR 101 ; MP 246.64 to 246.73, Vic. Black Diamond Road Bridge 101/340 Replacement Project, Port Angeles
1348755	Barnard, Kent M.	1991	Sunken Vessels and Aircraft Containing Hazardous Materials in Puget Sound
1348767	Daugherty, Richard D.	2006	An Archaeological survey of the Black Diamond Water District Property at the Little River
1349172	Gillis, Nichole A.	2007	Technical Memorandum: Cultural Resources Assessment during Geotechnical Drilling for the 8th Street Bridges Redesign project
1349873	Hodges, Charles	2007	Cultural Resources Assessment for the Port Angeles CSO Alternative 7
1349897	None Stated	2007	Letter to Jim Ulvenes RE: Cultural Significance of Deposits Observed during Monitoring at the Gateway Project Site, Port Angeles

Table 6-1 Results of Records Search conducted at the DAHP

NADB Number	Author	Date	Title
1350006	Wilt. Julia J.	2001	Results of a Cultural Resources Survey of the Bonneville Power Administration's Olympia to Port Angeles Fiber Optic Project Area
1350187	None Stated	2003	National Park Service Cultural Landscape Inventory, Park Headquarters, Olympic National Park
1350607	Stilson, M.L.	2007	Site Protection Plan for Port Angeles Western Rail Road Engine and Car Repair Shop and Creosote Removal Project
1350905	Lenz, Brett R.	2007	Geoarchaeological Analysis of the Hood Canal Bridge Graving Dock Site, Port Angeles

Table 6-2 Summary of Monitoring Efforts

Sample ID #	Sample Date(s)	Archaeologist	Findings	Photos
E106SS, E106RP	9/7/2008	McCollum	Isolated ceramics	2303, 2304, 2305, 2306, 2307, 2308, 2309, 2310, 2311, 2312, 2313, 2314, 2315, 2316
W208SS	9/10/2008	Pentney	No artifacts found	167, 168, 169
E302SS	9/10/2008	Pentney	No artifacts found	158, 159, 160, 161, 162
E101SS	9/10/2008	Pentney	No artifacts found, sample abandoned due to charcoal contamination	156,157
E299SS	9/9/2008	Pentney	No artifacts found	163,164,165,166
FF05SS	9/9/2008	McCollum	No artifacts found	2332, 2333, 2334
E117SS	9/9/2008	McCollum	No artifacts found	2339, 2340
E108SS	9/9/2008	McCollum	No artifacts found	2336, 2337
FF03SS	9/9/2008	McCollum	No artifacts found	2327, 2328, 2329
FF06SS	9/9/2008	McCollum	No artifacts found	2323, 2324
E201SS	9/9/2008	Pentney	No artifacts found	154, 155
W109SS	9/9/2008	Pentney	No artifacts found	150, 151, 152, 153
W108SS	9/9/2008	Pentney	No artifacts found	144, 145, 146, 147, 148
W215SS	9/9/2008	Pentney	No artifacts found	139, 140, 141, 142, 143
W306SS	9/9/2008	Pentney	No artifacts found	135, 136, 137, 138
E109SS	9/8/2008	McCollum	No artifacts found	340, 341, 343
T101SS	9/8/2008	Pentney	No artifacts found	120, 121, 122, 123
E405SS	9/8/2008	Pentney	No artifacts found	115, 116, 117, 118, 119
E206SS	9/8/2008	Pentney	No artifacts found	132, 133, 134
T302SS	9/8/2008	Pentney	No artifacts found	128, 129, 130, 131
E102SS	9/8/2008	McCollum	No artifacts found	350, 351
W201SS	9/8/2008	McCollum	No artifacts found	328, 329
W211SS	9/8/2008	McCollum	No artifacts found	315, 317, 320, 322, 325

Table 6-2 Summary of Monitoring Efforts

Sample ID #	Sample Date(s)	Archaeologist	Findings	Photos
W203SS	9/8/2008	McCollum	No artifacts found	39, 40, 41
FF02SS	9/4/2008	Pentney	No artifacts found	43, 44, 45
E406SS	9/4/2008	Pentney	No artifacts found	32, 33, 34, 35, 36
FF07SS	9/4/2008	Pentney	No artifacts found	37, 38, 39, 40, 41, 42
E208SS	9/4/2008	McCollum	No artifacts found	2213, 2214, 2215, 2216, 2217
FF04SS	9/4/2008	McCollum	No artifacts found.	2209, 2210, 2211, 2212
W301SS	9/6/2008	Pentney	One piece of terra cotta tile approx. 3.cm x 2.3.cm x 0.4 cm	103, 104, 105, 106, 107, 108, 109, 110
T103SS	9/12/2008	Pentney	1940s or 1950s Chrysler approx. 30 ft from sample area	211-217, 218, 219, 220, 221-224
T301SS	9/5/2008	Pentney	No artifacts found	75, 76 , 77 , 78
FF08SS	9/5/2008	Pentney	No artifacts found	60 , 61, 62, 63, 64, 65, 66
E204SS (multiple attempts at same location)		Pentney	No artifacts found	57, 58, 59
RD02SS	9/5/2008	Pentney	No artifacts found	47, 48, 49, 50, 51, 52
FF09SS	9/5/2008	McCollum	No artifacts found	2240, 2241, 2242
E103SS	9/5/2008	McCollum	No artifacts found	2223, 2224, 2225, 2226
RD01SS	9/5/2008	McCollum	No artifacts found	2232, 2233, 2234
E116SS	9/5/2008	McCollum	No artifacts found	2228, 2229, 2230
FF01SS	9/5/2008	McCollum	No artifacts found	2236, 2237, 2238, 2239, 2241, 2242
E121SS	9/5/2008	McCollum	No artifacts found	2219, 2220
W304SS	9/6/2008	McCollum	No artifacts found	2273, 2274, 2275, 2276
W204SS	9/6/2008	McCollum	No artifacts found	2244, 2245, 2247, 2248
W305SS	9/6/2008	McCollum	No artifacts found	2263, 2264, 2265
W302SS	9/6/2008	McCollum	No artifacts found	2267, 2270, 2271

Table 6-2 Summary of Monitoring Efforts

Sample ID #	Sample Date(s)	Archaeologist	Findings	Photos
W104SS	9/6/2008	McCollum	No artifacts found	2255, 2257, 2259, 2260, 2261
W209SS	9/6/2008	McCollum	No artifacts found	2250, 2251, 2252, 2253
W216SS	9/16/2008	Pentney	No artifacts found	97, 98, 99, 100
W202SS	9/6/2008	Pentney	No artifacts found	93, 94, 95, 96
W103SS	9/6/2008	Pentney	No artifacts found	87, 88, 89
W107SS	9/6/2008	Pentney	No artifacts found	90, 91, 92
W206SS	9/6/2008	Pentney	A piece of historic brick approx. 3.2 cm. x 3.8 cm. X 2 cm	79, 80, 81, 82, 83, 84
E110SS	9/7/2008	McCollum	No artifacts found	2299, 2300, 2301
W112SS	9/7/2008	McCollum	No artifacts found	2290, 2291
T201SS	9/7/2008	McCollum	No artifacts found	2278, 2280, 2282, 2283
E111SS	9/7/2008	McCollum	No artifacts found	2285, 2286, 2287, 2288
W212SS	9/7/2008	McCollum	No artifacts found	2295, 2296, 2297, 2298
W105SS	9/12/2008	Pentney	No artifacts found	200, 201, 202, 203, 204, 205
T102SS	9/12/2008	Pentney	No artifacts found, sample abandoned due to charcoal contamination	207, 208, 209, 210
T202SS	9/12/2008	Pentney	No artifacts found	228, 229, 230, 231, 232
W197SS	9/16/2008	Pentney	No artifacts found	284, 285, 286
W214SS	9/15/2008	Pentney	No artifacts found	280, 281, 282, 283
T203SS	9/15/2008	Pentney	No artifacts found	271, 272, 273, 274
T303SS	9/15/2008	Pentney	No artifacts found	267, 268, 269, 270
E205SS	9/15/2008	Pentney	No artifacts found, sample abandoned due to charcoal contamination	263, 264, 265, 266
E401SS	9/15/2008	Pentney	No artifacts found, sample abandoned due to charcoal contamination	259, 260, 261, 262
E196SS	9/15/2008	Pentney	No artifacts found	256, 257, 258
E195SS	9/15/2008	Pentney	No artifacts found	252, 253, 253, 255

Table 6-2 Summary of Monitoring Efforts

Sample ID #	Sample Date(s)	Archaeologist	Findings	Photos
E105SS	9/15/2008	Pentney	No artifacts found	248, 249, 250, 251
T104SS	9/15/2008	Pentney	No artifacts found	275, 276, 277, 278, 279
W205SS	9/14/2008	Pentney	No artifacts found	245, 246, 247
E198SS	9/14/2008	Pentney	No artifacts found	241, 242, 243, 244
E197SS	9/14/2008	Pentney	No artifacts found	237, 238, 239, 240
W198SS	9/14/2008	Pentney	No artifacts found	233, 234, 235, 236
E499SS	9/11/2008	Pentney	No artifacts found	170, 171, 172, 173
E199SS	9/11/2008	Pentney	No artifacts found	174, 175, 176, 177
W303SS	9/11/2008	Pentney	No artifacts found	178, 179, 180
W102SS	9/11/2008	Pentney	No artifacts found	184, 183, 182, 181
W213SS	9/11/2008	Pentney	No artifacts found	185, 186, 187, 188
W210SS	9/11/2008	Pentney	No artifacts found	189, 190, 191, 192
W207SS	9/11/2008	Pentney	No artifacts found	193, 194, 195, 196
W199SS	9/11/2008	Pentney	No artifacts found, sample abandoned due to charcoal contamination	197, 198, 199, 200
E122SS	11/10/08	Beery	No artifacts found	PA Nov Sampling 001-023
E194SS	11/10/08	Beery	No artifacts found	PA Nov Sampling 001-023
E298SS	11/10/08	Beery	No artifacts found	PA Nov Sampling 001-023
E403SS	11/10/08	Beery	No artifacts found	PA Nov Sampling 001-023
E498SS	11/10/08	Beery	No artifacts found	PA Nov Sampling 001-023
E402SS	11/11/08	White	No artifacts found	PA Nov Sampling 001-023
W196SS	11/11/08	White	No artifacts found	PA Nov Sampling 001-023
W299SS	11/11/08	White	No artifacts found	PA Nov Sampling 001-023

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Figures

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Figure 1-1. Sampled locations with artifacts

Figure 1-1 has been omitted from public drafts due to confidentiality laws.

Figure 6-1. E106SS isolated ceramics

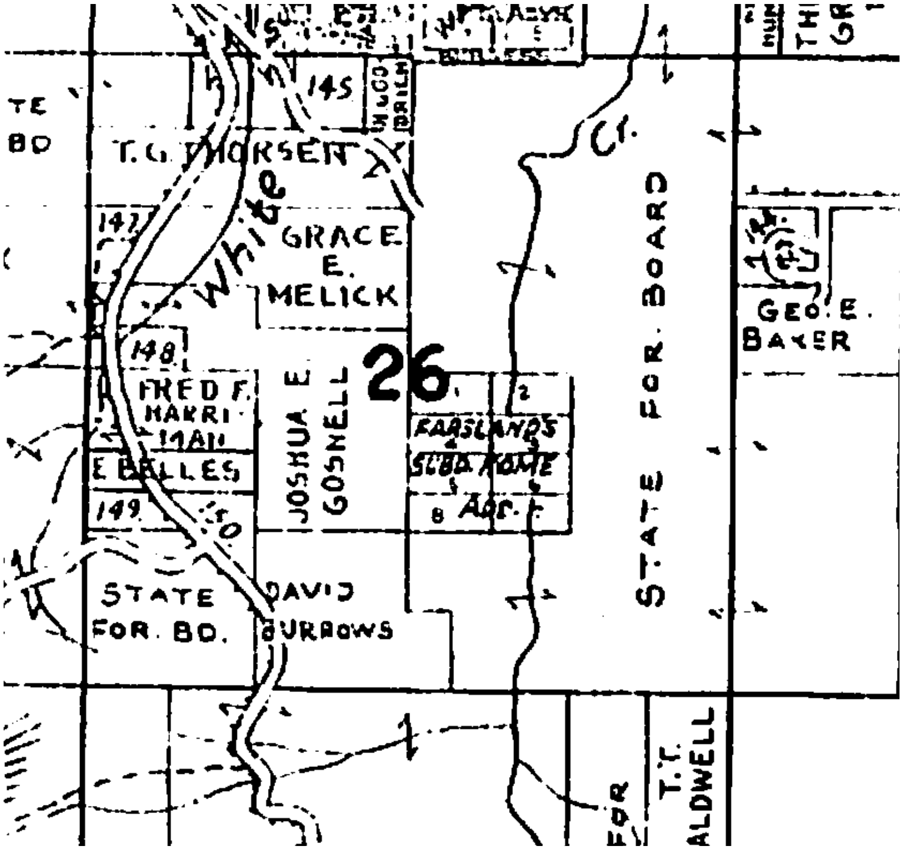
Figure 6-2. W301SS terracotta tile

Figure 6-3. W206SS red brick

Figure 6-4. T103SS historic road

Figure 6-5. T103SS abandoned automobile

Figure 7-1. 1955 road map of approximate T103SS artifact location



Appendix A: Site and Isolate Recording Forms

Appendix A has been omitted from public drafts due to confidentiality laws.

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B LABORATORY REPORTS, DATA VALIDATION REPORT, ELECTRONIC DATABASE

See attached disc.

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C SOURCE APPORTIONMENT STUDIES

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RAYONIER MILL OFF-PROPERTY SOIL DIOXIN STUDY

Source Apportionment Investigations

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January, 2011

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1. GLOSSARY

ALS – Alternating Least Squares, a mixture analysis algorithm for uncovering source patterns in a mixture and the corresponding contributions (source amounts) of the source patterns to the mixture samples

Correlation – a measure of association between two entities

Eigenvalue - the variance in a set of variables explained by an eigenvector

Eigenvector - linear combination of variables that has the greatest variance

HCA – Hierarchical Cluster Analysis, a method of displaying sample similarity in a dendrogram

Matrix decomposition – linear algebra methods to transform a data matrix into its underlying eigenvectors

Mixture analysis – a family of methods that aim to resolve a mixture into contributing end-members

Normalization – method of removing variation in a data vector by dividing by a standard factor such as the sum of values

Outlier – a sample in a data set that appears not to conform to the patterns of other samples

PCA – Principal Components Analysis, an algorithm for converting a matrix of measurements on a set of samples by defining new components as linear combinations of the original measurements

Pirouette – a commercial software package with tools for performing chemometrics analyses

Scaling – a method of scaling a measure across a set of samples to a common scale, such as variance

Score – a coefficient or measure of distance from a vector's mean such as that from an eigenvector

Standardization – a form of scaling on the values in a vector in which the mean is substracted from each value and the result is divided by the standard deviation

Source apportionment – use a mixture analysis algorithm to determine the contributions (also, source amounts) of underlying source patterns to samples

Variance - dispersion of a distribution about its mean

2. INTRODUCTION

Infometrix, Inc., was requested to participate in a study of dioxins in soils near the historical site of a pulp mill in Port Angeles, WA. In particular, the request was to include application of multivariate methods for the evaluation of important congeners of polychlorinated dibenzo-p-dioxins (dioxins) and dibenzofurans (furans) obtained from chemical analysis of soils collected in the region.

The relative concentrations of dioxin and furan congeners measured in Port Angeles soils reveals a pattern[1] that is distinct to emissions from hog fuel boilers using salt-laden wood. This observed pattern is ubiquitous in areas of eastern Port Angeles and is common in other in-town areas. The contribution of this pattern to areas further from the city is diminished, giving way to a more typical urban congener pattern.

No pattern of congeners from potential sources other than hog fuel boilers found in the scientific literature matches the profiles found in the sampling locations in the Port Angeles area. Patterns of some residential soils from other locations are similar to those found in a small number of sampled locations.

This report provides a brief introduction to the multivariate tools used in the study. A detailed description of the data analysis steps also is included.

---

[1] Pattern here refers to TEF-scaled amounts; see later text for details

3. MULTIVARIATE APPROACH

When a data analysis scenario includes the collection of more than one or two measurements, interpretation of results in a univariate sense (one variable at a time) can become tedious if not misleading. It is rare that measurements are completely independent (that is, selective); they are more commonly correlated. Univariate analysis cannot detect correlations and will misrepresent trends and relationships that result from correlation. Multivariate analysis uses tools and techniques from mathematics and statistics to guide interpretation of multichannel information, and the approach has been used in this study.

Among the multivariate tools used in the environmental field, factor-based and mixture analysis methods are the most common. Factor and principal components analysis are exploratory methods (Sharaf et al. 1986.; Beebe et al. 1998) that seek to find and understand relationships among samples, locate potential outliers or aberrant samples, and describe differences and similarities among measurements. Particularly suited to studies of source apportionment, mixture analysis algorithms (Johnson et al. 2007) such as target factor analysis, polytopic vector analysis and alternating least squares can reveal underlying patterns of chemical constituents and then assign contributions of these patterns to sample mixtures.

Data for multivariate analysis are usually composed in a rectangular matrix, with rows representing samples and columns representing measurements on these samples. This approach can be used for presenting for analysis the results of spectroscopic measurements, tables of chromatographic peak areas, or collections of discrete wet chemistry measurements. The patterns exhibited by the collection of measurements for each sample are like fingerprints, and the objective of environmental analysis is often to characterize the patterns in a collection of measured samples.

The dioxin and furan measurements in this study originate from chromatographic analyses. Although the chromatography used for the analyses is capable of resolving the vast majority of the 200-plus isomers of chlorinated homologs, it is customary in studies of these classes of compounds to focus on the 2,3,7,8-chloro isomers (Ecology 2007). This group of 17 compounds includes 7 dioxin and 10 furan isomers (see Section 4 on Data description and setup).

Detectors in chromatography do not respond in the same way to all compounds, thus peak intensities may vary considerably even when compounds are present in the same amounts. In addition, natural abundances of compounds that derive from a common source are expected to vary. As a result, the range of intensities of congeners can vary over several orders of magnitude. Finally, the actual concentration of material injected into the gas chromatograph cannot be perfectly controlled.

If a multivariate analysis were to be performed on raw patterns of data in which the measurements vary by such large amounts, those compounds with the largest intensity would drive the analysis. In other words, the analysis would reflect only the information in the most abundant measures. To allow interpretation of the differences in chromatographic fingerprints, it is customary to scale the data to put all measurements on a common scale.

The first step in standardizing data is to scale the individual measurements to be of similar magnitude. In most chemometric studies in which the measurements are discrete and not continuous, each measurement is scaled by either the range or the standard deviation of the measure across all samples.

The result is that each scaled variable will either have a range of 0 to 1 or a variance of 1. There are two drawbacks to these scaling methods: (1) the scaling factor is a function of the samples that are included in the calculation and would therefore change if different samples were processed, and (2) there is a risk that a variable of little importance and of intensities in the noise level will be magnified to the same importance as variables with real, diagnostic signal.

One method frequently used in studies of dioxins (see, for example, Lohmann and Jones 1998; Alcock et al. 2002; Hilscherova et al. 2003; and Demond et al. 2008), and used here, is to scale by a toxic equivalency factor (TEF; see Table 3), based on toxicities relative to 2,3,7,8-TCDD. An advantage of TEF scaling not shared by the other methods is that the result is not dependent on the particular data set because the scaling is done for each sample independently. The scaling factors for range and variance scaling are derived from calculations using all of the data; changing what data are included will change the scale factors.

The second step is to normalize by area percent (divide each value in a sample by the sum of the TEF-scaled values in that sample). Relative differences in amount of material entering the chromatogram are thus removed, allowing comparison of patterns without complications of sample amount.

Factor analysis (FA) and principal components analysis (PCA) are two exploratory algorithms that share code and objectives, differing very little in use (Massart et al. 1988). The essence of each is the concept that the number of measured variables determines the dimensionality of a data set. If there are two variables measured, data can be plotted on an X-Y plot and relationships can easily be visualized. A 3-dimensional plot with X, Y, and Z axes can present data from three measurements. But, beyond three measurements, it rapidly becomes cumbersome to visualize data in plots.

It is possible to rotate the axes: instead of using the measurements to define the axes, we can take advantage of correlation among the variables and use different combinations of variables to force the axes into different positions. The axes remain orthogonal to each other but there are still as many 'new' axes as there were before. A special way of choosing which directions these new axes take is based on results from PCA: the first new axis is oriented in the direction of maximum spread in the data on the original measurement axes. Thus, a linear regression through the data points will result in a line that would become the first "eigenvector", the name often used to designate the new axis. After removing the effect of this first new direction (by projecting all points onto this line and looking at what is left), another regression is done to find the next new direction of maximum spread, forming the second eigenvector. This is repeated until a whole new set of axes is defined.

Because each step of the matrix decomposition finds the variance in the current matrix, each eigenvector has associated with it the amount of variance it describes. And, because each successive step has less variance to work with, the variance explained in the eigenvectors decreases monotonically. Depending on the data set, the amount of variance described in just the first few eigenvectors will rapidly approach 100%. Thus, a data set with many dimensions (for example, a data matrix measured on the 17 congeners is a 17-dimensional set) can be reduced to what is practically a redefined set of much reduced dimensionality, perhaps as little as 3 or 4 eigenvectors, and we can safely ignore the remaining directions which represent only a fraction of the total variance, say less than 1% or 0.1%.

Relationships among the samples do not change when axes are rotated. However, their positions on the new axes, referred to as scores, will be different. The relationships among the samples will usually become much more understandable by reducing the complexity of the data to just a few coordinates.

Unfortunately, the eigenvectors do not have physical meaning; they are abstract vectors derived only from variation in the data. Observation of the scores can help guide an interpretation such as that there may be groups of similar samples, or even that there are samples that are located in positions intermediate between others, implying that they might be mixtures. But, to do source apportionment, we need a tool to find those patterns that appear to underlie all of the mixed samples and have physical meaning.

Mixture analysis algorithms are designed to find those patterns. Although there are many different algorithms for doing mixture analysis, their objectives are similar: extract the patterns from which the sample mixtures are composed. The alternating least squares (ALS) approach used in this study may differ from the approach used in other methods (Johnson et al. 2007), but results are generally comparable.

First, we assume that a matrix of data (whose dimension is number of samples down the rows by number of measurements across the columns) derived from a single material can be built by multiplying the vector (or list) containing the amounts of this material in the different samples by the vector that represents the pattern of measurements for that material. If there are two materials, then the data would be formed by multiplying a table of compositions (of size number of samples by the two columns of compositions of the two materials) by the table containing the two patterns (one row of numbers for each material). Data originating from more than two sources would come from similarly larger composition and profile tables.

The ALS algorithm (Tauler et al. 1993) works by trying to discover these two matrices of compositions and patterns. This can be restated as solving a single equation with two unknowns, which of course cannot be solved directly. Instead, one matrix, say that of the patterns, is estimated first and, using matrix algebra, an estimate is then derived for the other matrix, that of the compositions. Then this estimated matrix of compositions is used to deduce a matrix of the patterns. If no other intervention was done, we would be back where we started.

To assure that we get closer to a meaningful solution, before the two estimation steps are repeated, constraints are applied to the newly estimated data. There are many forms the constraints can take, but the most common are to apply non-negativity to both matrices: we assume that the intensities in the measurements cannot be less than zero, and we also assume that the proportions of the two patterns that make up the compositions must also be zero or positive. By applying these constraints, the iterations through the steps of estimating first the patterns matrix and then the compositions matrix will eventually converge to a solution where the patterns and compositions are meaningful.

4. DATA DESCRIPTION AND SETUP

Data were submitted to Infometrix in the form of an Excel spreadsheet containing analyte concentration for each sampling location, plus summary data and data corrected for TEFs, both arranged in matrix form, congeners versus sampling locations. TEF-modified congener concentrations can be summed to obtain a toxic equivalent concentration (TEQ) for each sample. The two non-normalized matrices, referred to as the Data Summary and Data Summary TEQ matrices, were manipulated to retain the following components:

- the 17 congeners;
- non-detect values;
- total organic carbon (TOC);
- sample type descriptor;
- distances from Rayonier boiler site, in feet and in degrees; and
- geographic coordinates, in NAD 83 Washington State Plane North (feet)

The raw Data Summary also retained the total homologs. Each matrix was saved to a separate file, also in Excel format. Sample type was converted to numerical values, in the following mapping[2]. Plots will use this color mapping unless specified differently.

Table 1. Sample type categories

Sample type	Category	Color
Grid	1	🟦
Forested	2	🟩
Road	3	🟥
Transect	4	⬛

The massaged tables were imported into Pirouette. The sample type variable was made into a categorical variable, and the non-detect values, distances and coordinates were made into dependent variables. Colors were assigned to the category values as shown in the above table, such that any sample-oriented plots could be evaluated on the basis of sample type. Finally, the TOC and Total homolog variables were excluded so that only the 17 congener values were included for subsequent multivariate analysis. In Table 2[3], this information is presented for the 85 samples in the study.

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[2] Correct sample type designations were used in data interpretations; sample design codes were retained for consistency when tracking sample site information. A few samples were recoded to 'forest' type.

[3] The X and Y values in this table are the geographic coordinates (NAD83). Samples are in alphabetical order, grouped roughly by sample design codes. One sample (E112SS) was miscoded as W112 in the field and is still shown with the W-coded samples but with the corrected designation. Note that several samples not initially coded as forest samples are carried through the analyses as forest-type samples.

Table 2. Samples IDs and information

Index	ID	Type	TEQ	X	Y
1	E102SS	1	15.18	470286	5328801
2	E103SS	1	16.47	470159	5328802
3	E105SS	1	14.29	470670	5328717
4	E106SS	1	17.74	470525	5328484
5	E108SS	1	13.76	470772	5328634
6	E109SS	1	26.24	470600	5328490
7	E110SS	1	4.15	470709	5328277
8	E111SS	1	12.76	470726	5328997
9	E116SS	1	6.30	471014	5328975
10	E117SS	1	10.95	470953	5328668
11	E121SS	1	3.40	471089	5328573
12	E122SS	1	10.45	471269	5328359
13	E194SS	1	5.94	470047	5329036
14	E195SS	1	9.44	470020	5328937
15	E196SS	1	2.54	470253	5328565
16	E197SS	1	26.62	470527	5328997
17	E198SS	1	14.31	470851	5328995
18	E199SS	1	6.60	470081	5328621
19	E201SS	1	15.10	471382	5328600
20	E204SS	1	5.05	472369	5328614
21	E206SS	2	9.18	472974	5328918
22	E208SS	1	3.84	473231	5329061
23	E298SS	1	7.87	472957	5328877
24	E299SS	1	8.29	471345	5328924
25	E302SS	1	4.14	470679	5327332
26	E402SS	2	4.06	472687	5326968
27	E403SS	2	40.46	473012	5327480
28	E405SS	1	7.63	474132	5328768
29	E406SS	1	6.45	474214	5329249
30	E498SS	2	7.69	472870	5327815
31	E499SS	1	19.90	474128	5329074
32	FF01SS	2	27.13	473774	5327860
33	FF02SS	2	9.10	474014	5328019
34	FF03SS	2	7.89	473420	5328793
35	FF04SS	2	18.41	473186	5328913
36	FF05SS	2	4.02	472927	5328033
37	FF06SS	2	25.58	472077	5328754
38	FF07SS	2	14.96	471712	5327679
39	FF08SS	2	6.41	472840	5327681
40	FF09SS	2	34.17	472809	5329107
41	RD01SS	3	6.50	473507	5327795
42	RD02SS	3	4.04	472523	5328128
43	T101SS	4	1.82	468637	5325190
44	T103SS	4	2.19	468784	5324055
45	T104SS	4	2.39	468215	5326105

Index	ID	Type	TEQ	X	Y
46	T201SS	4	5.54	470402	5324673
47	T202SS	4	1.29	470800	5324098
48	T203SS	4	2.37	470731	5323287
49	T301SS	4	1.67	472948	5325194
50	T302SS	4	0.80	472661	5324675
51	T303SS	4	1.20	472192	5323647
52	W102SS	1	10.68	468535	5329376
53	W103SS	1	8.41	468793	5329310
54	W104SS	1	15.24	469135	5329004
55	W105SS	1	17.11	469287	5329076
56	W107SS	1	26.26	469423	5329001
57	W108SS	1	8.60	469553	5328714
58	W109SS	1	9.66	469692	5328692
59	E112SS	1	18.17	470893	5328791
60	W196SS	1	1.13	468895	5329317
61	W197SS	1	22.14	469552	5329042
62	W198SS	1	22.06	468911	5329147
63	W201SS	1	11.40	468266	5329068
64	W202SS	1	12.92	468059	5328771
65	W203SS	1	23.19	467571	5328305
66	W204SS	1	17.45	468573	5328952
67	W205SS	1	10.20	468339	5328567
68	W206SS	1	13.83	467976	5328299
69	W207SS	1	13.72	468907	5328610
70	W208SS	1	5.87	468733	5328323
71	W209SS	1	76.26	468324	5327981
72	W210SS	1	25.56	469191	5328436
73	W211SS	1	1.76	469003	5328266
74	W212SS	1	5.93	468693	5328017
75	W213SS	1	28.78	469402	5328339
76	W214SS	1	27.60	469891	5327761
77	W215SS	1	6.92	469869	5328140
78	W216SS	1	17.45	469786	5327701
79	W299SS	2	12.04	468919	5328070
80	W301SS	1	11.73	466876	5329733
81	W302SS	1	13.16	466138	5328736
82	W303SS	1	11.21	467365	5329438
83	W304SS	1	23.73	467014	5328989
84	W305SS	1	4.57	468165	5329459
85	W306SS	1	12.00	467067	5328460

The order of presentation of the congeners does not impact the data analysis, however, the order customarily used in studies of this type—increasing chlorination and increasing substitution position—was imposed and is shown in Table 3.

Table 3. Congener names and toxic equivalency factors

Index	Congener	TEF
1	2,3,7,8-TCDD	1
2	1,2,3,7,8-PECDD	1
3	1,2,3,4,7,8-HXCDD	0.1
4	1,2,3,6,7,8-HXCDD	0.1
5	1,2,3,7,8,9-HXCDD	0.1
6	1,2,3,4,6,7,8-HPCDD	0.01
7	OCDD	0.0003
8	2,3,7,8-TCDF	0.1
9	1,2,3,7,8-PECDF	0.03
10	2,3,4,7,8-PECDF	0.3
11	1,2,3,4,7,8-HXCDF	0.1
12	1,2,3,6,7,8-HXCDF	0.1
13	1,2,3,7,8,9-HXCDF	0.1
14	2,3,4,6,7,8-HXCDF	0.1
15	1,2,3,4,6,7,8-HPCDF	0.01
16	1,2,3,4,7,8,9-HPCDF	0.01
17	OCDF	0.0003

5. DATA ANALYSIS

Preliminary evaluation of the appropriateness of the data was conducted via line plots and principal components analysis (PCA). These steps often allow identification of unusual or aberrant samples that should be excluded from processing; retaining outlier samples can influence subsequent interpretation.

For example, the data from the Data Summary matrix are shown in Figure 1 as a line plot. This graphic shows the bulk congener data without any scaling of the response values. Each trace in this plot presents the values for each congener (some presentations of this type of data use bar or column charts; with large numbers of samples, however, those forms of presentation become difficult to interpret).

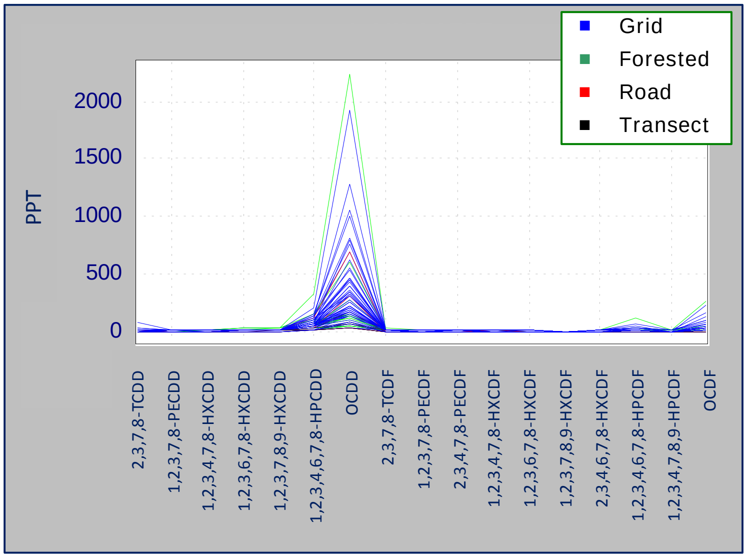

Figure 1. Bulk congener data profiles of all study samples overlaid

Many analyses of congener data have, in the past, worked only with the bulk congener values. Because these data range over four orders of magnitude, typical chemometric analysis is to apply some form of scaling. Both approaches—scaling and not scaling—will be considered in this study.

One form of scaling of dioxin/furan data sets is by the TEF values (shown in Table 3). This normalization will reduce the range in values by an order of magnitude. However, as shown in Figure 2, one sample shows an unusually large value for the first congener, 2,3,7,8-TCDD, with a value of 72 while the next-highest value is only 22.

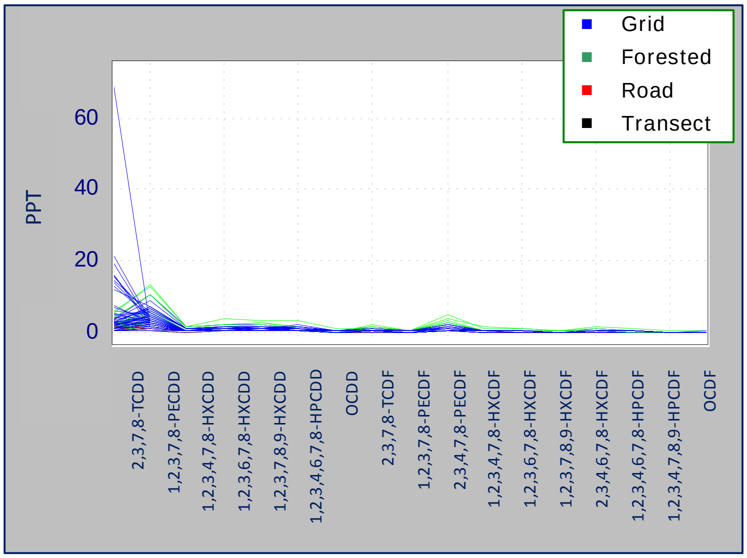

Figure 2. Line plots of all TEQ samples overlaid

A plot of the PCA scores[4] of this same data matrix (Figure 3) also shows this sample (W209SS) to be significantly different than all other samples. A single unusual sample such as this can have an undue influence on multivariate computations, therefore, this sample was excluded from subsequent analyses.

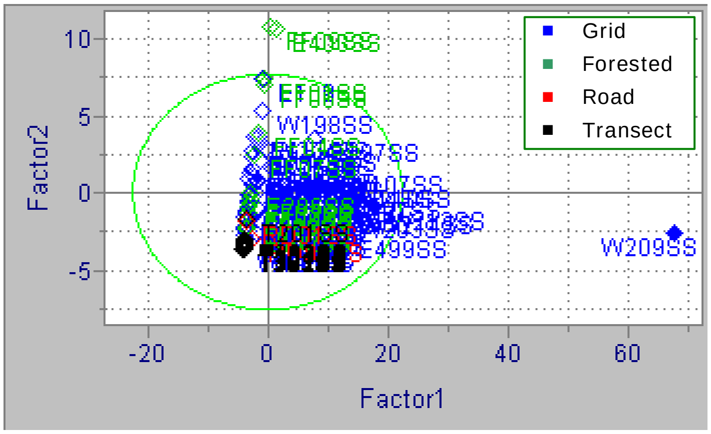

Figure 3. PCA Scores of all samples using 17 congener TEQ data

In addition to scaling dioxin and furan data (e.g., by TEF values), it is customary to further normalize the data to account for varying sample sizes such that absolute concentration is minimized. Although many different methods of normalization are used in the multivariate field, area % normalization is typical for chromatography data and was used in this study. Figure 4 shows area % normalized TEQ data.

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[4] The green ellipsoid in this and subsequent 2-D scatter plots is a 95% confidence boundary for the sample set analyzed.

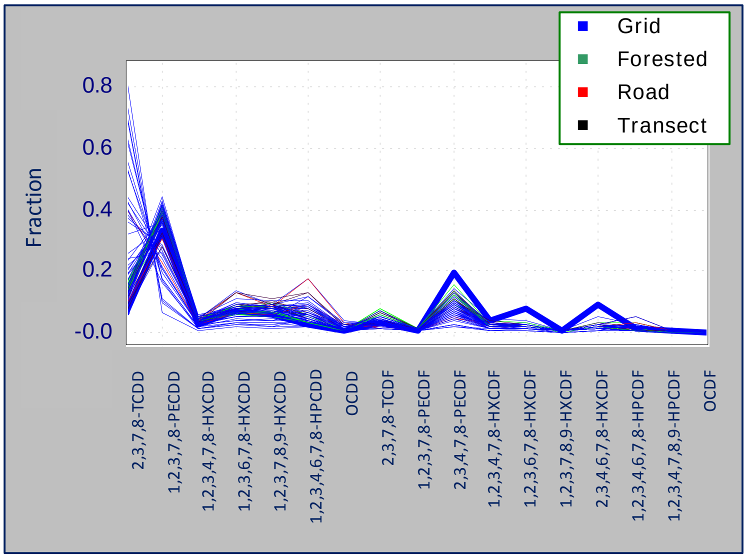

Figure 4. Area % normalized congener profiles, excluding sample W209SS

This figure shows most congener intensities to be within 2 orders of magnitude which means that the more intense (scaled) congeners will have a reduced tendency to influence the multivariate processing. PCA was also run on this normalized subset, and the scores are shown in Figure 5.

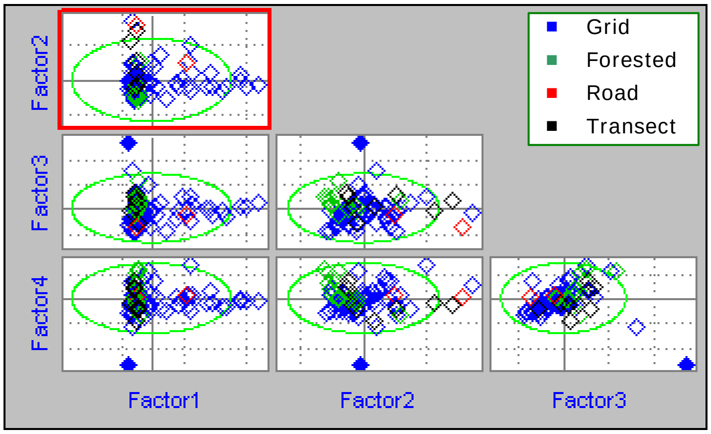

Figure 5. PCA scores of area % normalized congener profiles

From this view, it is clear that another sample (E406SS, the filled point in Figure 5) is unusual, in both the factor 3 and factor 4 directions. The line plot in Figure 4 shows this sample as a thicker blue trace and indicates how this sample differs from others, particularly for the furans. A plot of outlier diagnostics (Figure 6) more clearly shows that this is an aberrant sample.

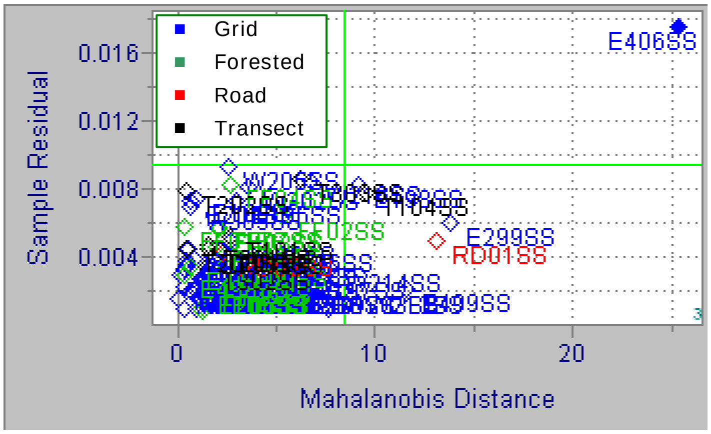

Figure 6. PCA outlier diagnostics of congener data

A way to view how this sample differs, that is, what variables cause the difference, is through a plot of the error contributions, as shown in Figure 7.

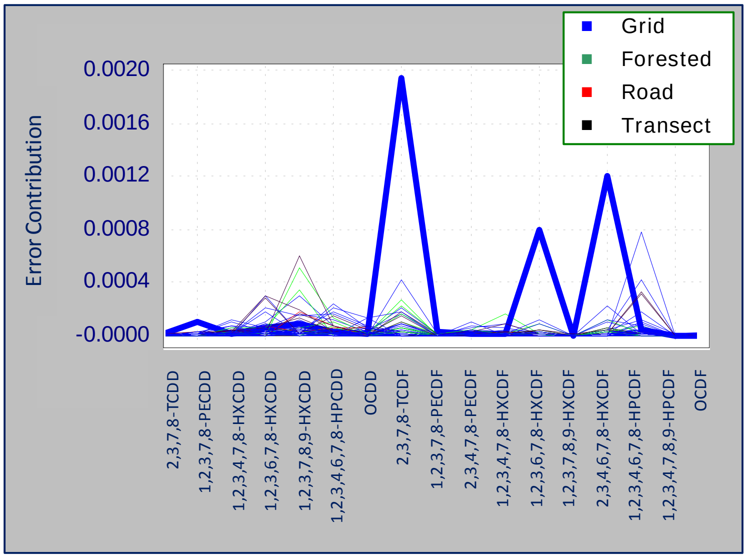

Figure 7. PCA error contributions of congener data

Again, the thicker line in the plot is for the sample highlighted in Figure 5 and Figure 6. This view emphasizes the unusual nature of the sample and shows that for three congeners, values were significantly higher. For the same reasons as for sample W209SS, this sample was also excluded from subsequent analyses.

The trimmed data subset (83 samples) was subjected to mixture analysis using the ALS algorithm. As part of this algorithm, a PCA is also performed (in this case, no centering is applied as it would conflict with the non-negativity constraint of ALS). The eigenvalues from the PCA are shown in Table 4.

Table 4. PCA eigenvalues (as variance) of scaled TEQ congener data

Factor	Variance	Percent	Cumulative
1	15.462	81.174	81.174
2	3.391	17.801	98.975
3	0.143	0.749	99.725
4	0.033	0.174	99.898
5	0.008	0.042	99.940
6	0.004	0.024	99.964

The scores from this analysis (Figure 8) show there is dispersion in at least three directions, an indication that there are at least three underlying factors responsible for the different compositions.

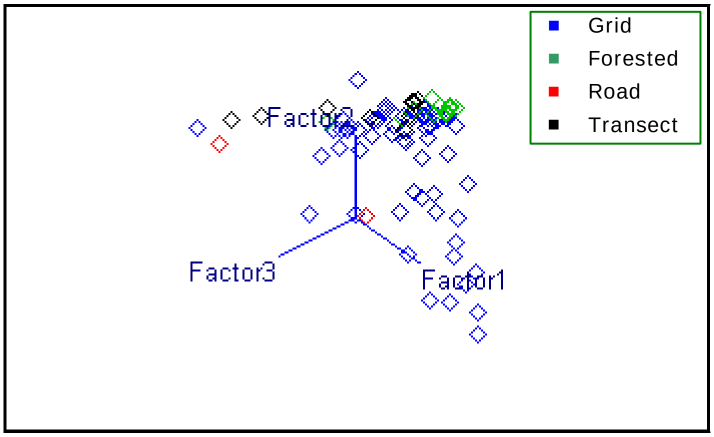

Figure 8. PCA scores of congener data

The corresponding PCA loadings are shown Figure 9. It is difficult to assign physical meaning to each of the loading profiles because the determination of the loading shape is based on describing variance in the data matrix and not from any prescribed attributes. In addition, some of the loading values are negative, an unreasonable shape for real profiles.

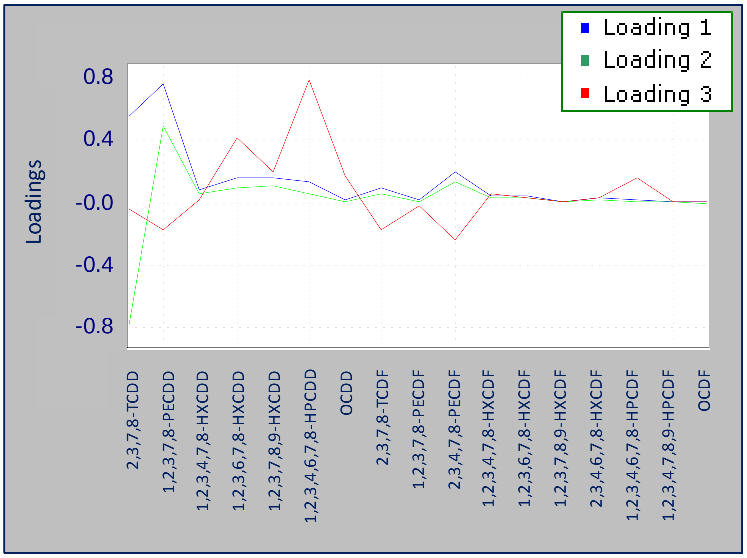

Figure 9. PCA Loadings of congener data

It is possible to create other combinations of vectors to represent the data matrix; in fact the number of possible combinations is infinite. This is referred to as rotational ambiguity and is why other algorithms are applied to seek an unambiguous solution.

The ALS algorithm, via the constrained method described in Section 3, computes two fundamental matrices: the underlying profiles of congener patterns and the proportional contributions of these profiles to the sample compositions. The profiles developed from ALS are not the same as those from PCA (that is, the loadings). Ideally, the profiles represent legitimate patterns for the sources of different materials present in the mixtures. The number of possible sources is determined by examination of the magnitude of the eigenvalues and by physical interpretation of the source profiles.

Figure 10 shows the ALS solution for 3 different sources. Based on the dispersion of samples in the scores shown in Figure 8, an ALS solution considering only 2 sources was not pursued.

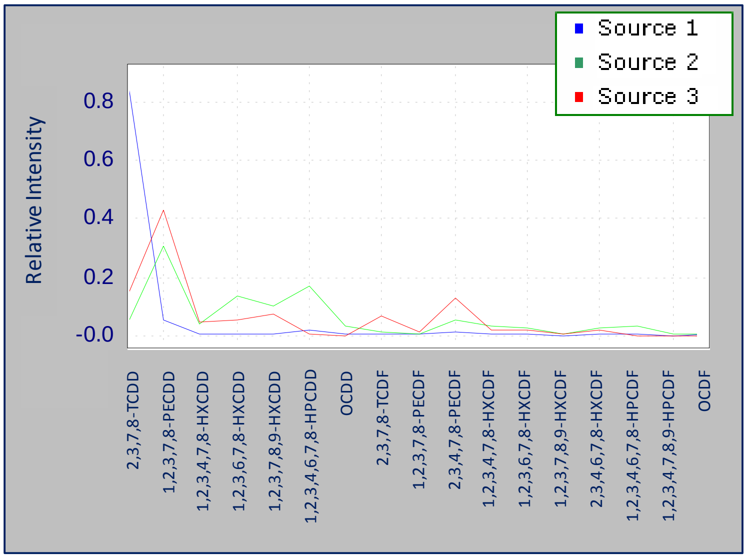

Figure 10. ALS source profiles for congener data

These profiles show significant differences in the proportions of the different congeners. One source (shown in blue) is composed almost exclusively of the first congener, 2,3,7,8-TCDD, a second is composed primarily of only dioxin congeners, and a third is a blend of lower chlorination dioxins and furans.

Corresponding to the profiles are the fractional contributions of each to the sample composition, shown in Table 5. Because this ALS analysis was run with a closure constraint, the proportions for each sample sum to 1.

Table 5. Source amounts from ALS on trimmed data set

	Source 1	Source 2	Source 3
E102SS	0.237	0.165	0.598
E103SS	0.327	0.269	0.403
E105SS	0.002	0.322	0.676
E106SS	0.065	0.322	0.613
E108SS	0.027	0.499	0.474
E109SS	0.016	0.245	0.740
E110SS	0.018	0.506	0.476
E111SS	0.016	0.247	0.738
E116SS	0.000	0.222	0.778
E117SS	0.000	0.297	0.703
E121SS	0.036	0.379	0.585
E122SS	0.411	0.203	0.387
E194SS	0.019	0.194	0.786
E195SS	0.020	0.547	0.433
E196SS	0.032	0.348	0.620
E197SS	0.420	0.152	0.428
E198SS	0.000	0.279	0.721
E199SS	0.096	0.319	0.585
E201SS	0.000	0.243	0.758

	Source 1	Source 2	Source 3
E204SS	0.094	0.423	0.483
E206SS	0.007	0.202	0.791
E208SS	0.000	0.240	0.760
E298SS	0.031	0.387	0.582
E299SS	0.033	0.967	0.000
E302SS	0.029	0.214	0.757
E402SS	0.013	0.242	0.746
E403SS	0.072	0.508	0.420
E405SS	0.346	0.199	0.455
E498SS	0.036	0.288	0.675
E499SS	0.962	0.030	0.008
FF01SS	0.028	0.300	0.672
FF02SS	0.023	0.087	0.890
FF03SS	0.040	0.131	0.829
FF04SS	0.025	0.068	0.908
FF05SS	0.006	0.203	0.791
FF06SS	0.025	0.127	0.849
FF07SS	0.020	0.103	0.878
FF08SS	0.022	0.119	0.859
FF09SS	0.017	0.090	0.894
RD01SS	0.055	0.945	0.000
RD02SS	0.409	0.438	0.153
T101SS	0.028	0.490	0.482
T103SS	0.003	0.184	0.813
T104SS	0.046	0.852	0.102
T201SS	0.005	0.209	0.786
T202SS	0.035	0.395	0.571
T203SS	0.029	0.261	0.710
T301SS	0.007	0.198	0.795
T302SS	0.043	0.334	0.623
T303SS	0.002	0.769	0.229
W102SS	0.128	0.288	0.584
W103SS	0.027	0.284	0.689
W104SS	0.101	0.224	0.674
W105SS	0.135	0.210	0.655
W107SS	0.593	0.146	0.261
W108SS	0.024	0.312	0.664
W109SS	0.038	0.516	0.446
E112SS	0.000	0.358	0.642
W196SS	0.011	0.586	0.404
W197SS	0.687	0.125	0.189
W198SS	0.054	0.244	0.702
W201SS	0.044	0.277	0.679
W202SS	0.458	0.273	0.269
W203SS	0.811	0.137	0.052
W204SS	0.028	0.201	0.771
W205SS	0.229	0.533	0.239
W206SS	0.140	0.507	0.353
W207SS	0.561	0.117	0.323

	Source 1	Source 2	Source 3
W208SS	0.082	0.350	0.568
W210SS	0.675	0.063	0.263
W211SS	0.062	0.438	0.500
W212SS	0.430	0.448	0.122
W213SS	0.851	0.047	0.102
W214SS	0.812	0.188	0.000
W215SS	0.183	0.249	0.568
W216SS	0.446	0.554	0.000
W299SS	0.048	0.140	0.812
W301SS	0.014	0.156	0.829
W302SS	0.108	0.184	0.708
W303SS	0.059	0.211	0.731
W304SS	0.590	0.284	0.127
W305SS	0.167	0.434	0.400
W306SS	0.391	0.210	0.399

The source amounts are perhaps more easily understood in graphical form. In Figure 11, each trace represents the values (magnitude of contribution) for one source as a function of sample site, where trace colors for the source amounts match the trace colors for the source profiles shown in Figure 10. The Sample Index in this plot corresponds to Table 2.

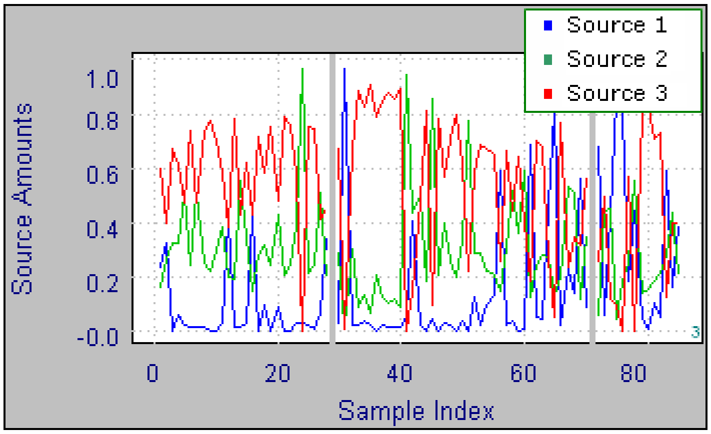

Figure 11. ALS source amounts for congener data

From this figure, it appears that the source shown in red (Source 3) is the most abundant contributor to the sample composition, deriving from the corresponding (red) source profile of Figure 10. A 3-source solution can also be viewed in a ternary plot as in Figure 12. In this plot, it is seen that the majority of samples fall near the vertex for Source 3, confirming the information in Figure 11.

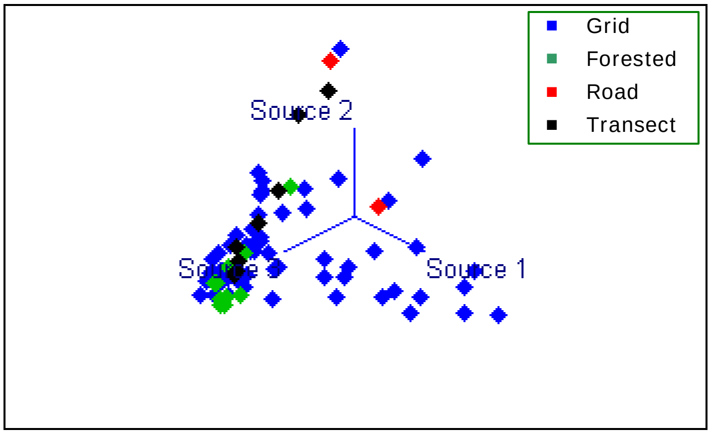

Figure 12. Ternary plot of congener source compositions

When doing source apportionment, the algorithm is attempting to fit structure to the data in a way that best characterizes the data. By looking at the residuals from this fit, that is, the information that is not included in accomplishing the apportionment, we can get an idea of how well the fit succeeded. Figure 13 shows the residuals for each sample.

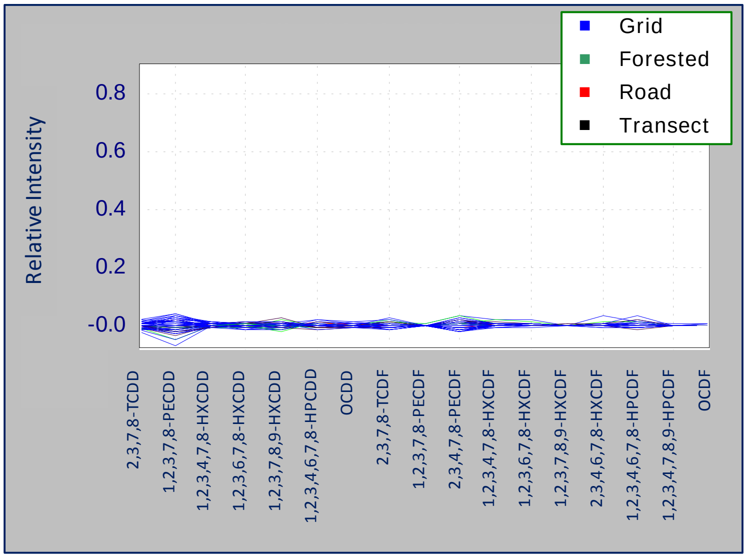

Figure 13. Residuals from an ALS model of 3 sources

This plot has been scaled to the same y-axis limits as that of Figure 4 to illustrate the relatively small magnitude of the ALS model residuals, which demonstrates a good quality fit to the TEQ congener data.

The possibility that 4 sources are contributing was also considered; the source profiles for this scenario are shown in Figure 14.

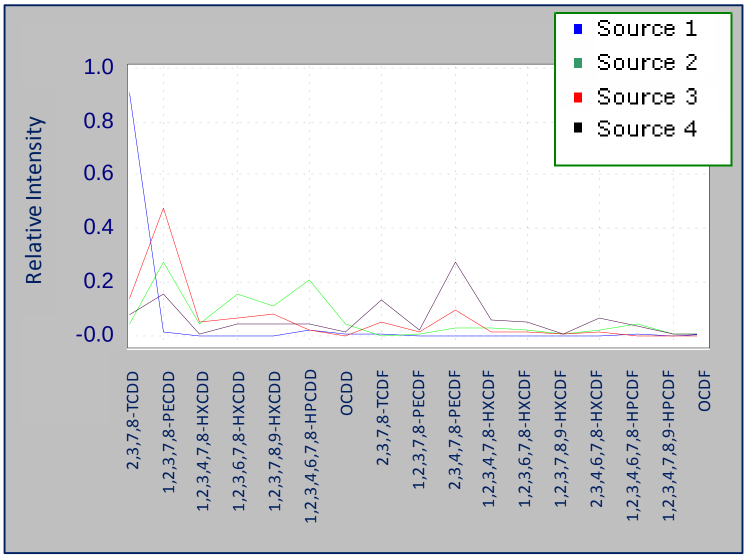

Figure 14. Source profiles for a 4-source ALS solution

Comparing this result to a 3-source solution (see Figure 10), the new profile (in black) is composed predominantly of two furans: 2,3,7,8-TCDF and 2,3,4,7,8-TCDF. The other profiles are changed only slightly, mostly by a reduction in the proportions of these two furans.

The corresponding source contributions for a scenario with 4 sources is shown in Figure 15. The new amounts from source 4 are emphasized by the thicker trace (black) in the plot.

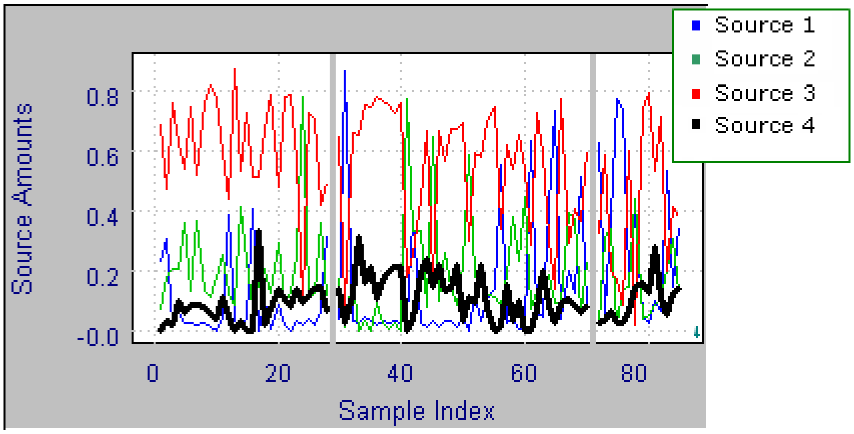

Figure 15. Source amounts for a 4-source ALS solution

Because the contributions from Source 4 to each of the samples are relatively low (mostly below 20%) and have only a small impact on the preponderance of the contributions from the other sources (see Figure 11), it is questionable whether a 4-source solution is warranted. Subsequent interpretations were based on a 3-source scenario.

In addition to the analyses run on TEF-scaled data, other analyses were run on the same data scaled by range and by variance. Other treatments (normalization, algorithm settings) were the same. Results from

ALS mixture analysis on the two scaling treatments were essentially the same; results shown below are those for variance-scaling only.

Based on the amount of variance explained and interpretation of the source contributions to the sample mixtures, either 5 or 6 sources seems appropriate for an ALS analysis with variance-scaled data. However, Source 2 (see Figure 16) consists of essentially a single sample (W196SS).

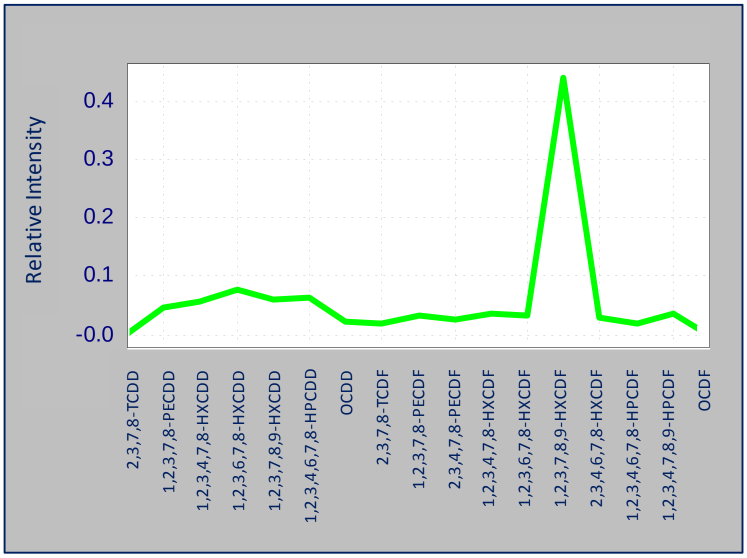

Figure 16. Source 2 profile from ALS on variance-scaled data

Because this sample has very low levels of all congeners, when it is scaled by range or variance, then normalized, the intensity at 1,2,3,7,8,9-HXCDF is highly emphasized, making this sample appear peculiar relative to all other samples, as shown in Figure 17 (sample W196SS trace is the thicker blue line).

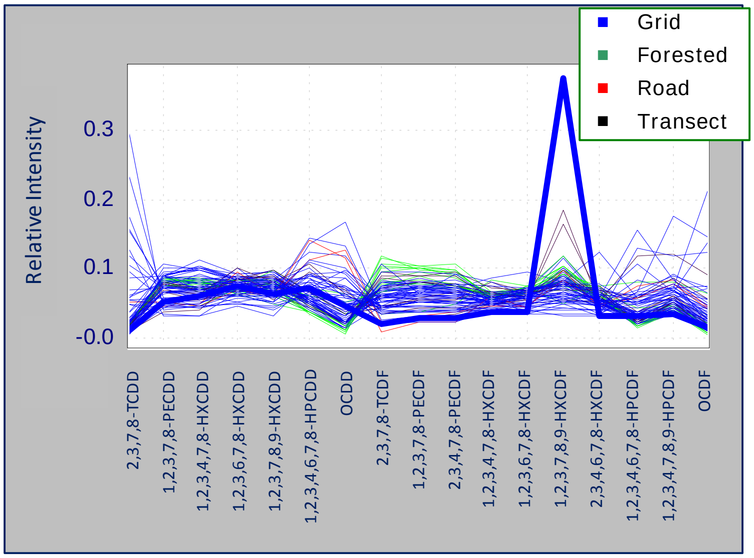

Figure 17. Unusual intensity for sample W196SS after variance scaling and normalization

The situation of low intensities having undue influence on multivariate analysis is one of the drawbacks of using a scaling method that treats all variables alike; this problem is often cited in the chemometrics literature. However, source allocations among the remaining samples were essentially the same as that resulting from ALS run on the TEF-scaled data. Remaining analyses were performed on TEF-scaled data.

6. DISCUSSION

6.1. SPATIAL TREND ANALYSES

Overall TEQ shows only a small correlation to distance or direction from the hog fuel boiler when looking at all samples at once, as shown in Figure 18.

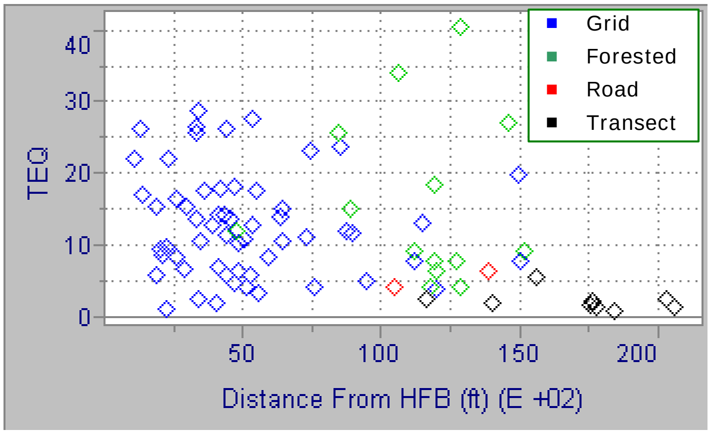

Figure 18. TEQ as a function of distance from hog fuel boiler (HFB)

However, noting that the prevailing wind direction in the Port Angeles area is easterly (Ecology 2008), a trend of diminishing dioxin amounts as a function of distance may be apparent when considering non-forested sample sites most likely to be in the effluent path. Figure 19 through Figure 24 show this trend by focusing on sample locations that fall within narrow wedges of cardinal directions with the hog fuel boiler as a proposed source location. Thus, the plots show only the subset of sample points that match the coordinate directions shown in the figure caption.

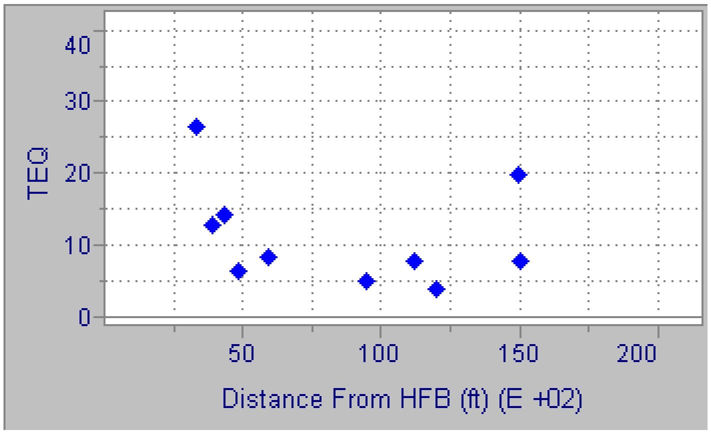

Figure 19. TEQ vs. distance for E-ESE non-forested samples

The dropoff in dioxin level with distance is more pronounced when considering individual congeners. For example, 1,2,3,7,8-PCDD is a prevalent peak in the patterns noted for proposed Sources 2 and 3. Plotting this congener as a function of distance for samples in the east to east-southest direction (non-forested samples only) shows a decreasing trend (see Figure 20). Similar trends are also evident in the other predominant dioxin congeners, also in Figure 20, and furan congeners, in Figure 21.

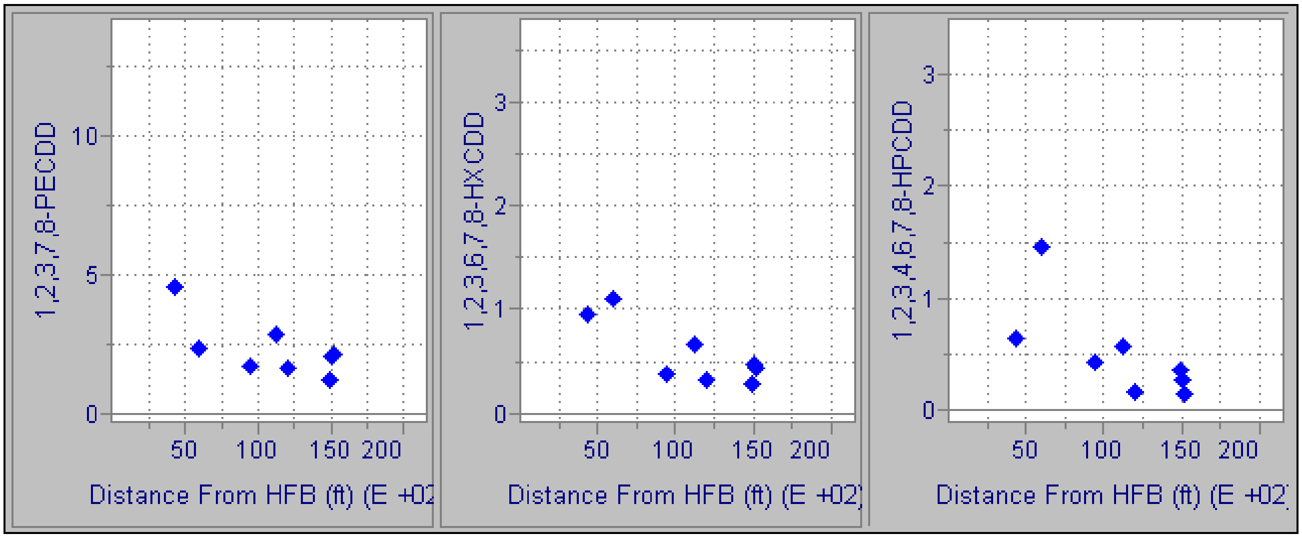

Figure 20. Congener response (selected dioxins, as TEQ) vs. distance from boiler for non-forested samples in E-ESE direction

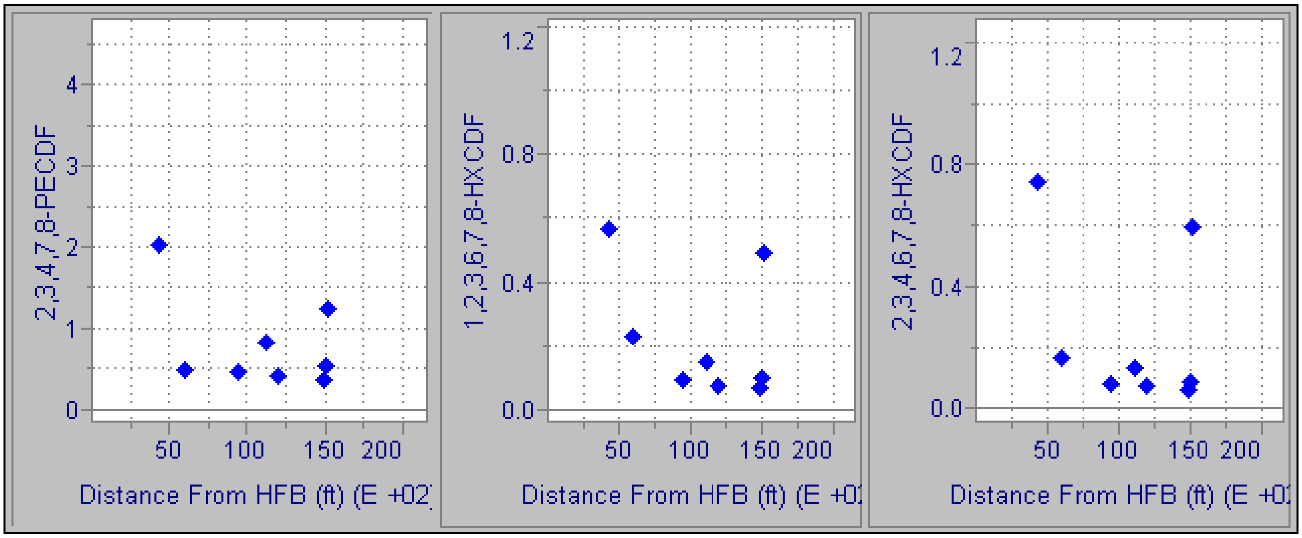

Figure 21. Congener response (selected furans, as TEQ) vs. distance from boiler for non-forested samples in E-ESE direction

This trend is not so clear, however, in non-forested samples in the east-southeast to southeast path, as shown in Figure 22. But, because these sampling sites are located in a fairly narrow region, there may not be enough distance to exhibit a trend.

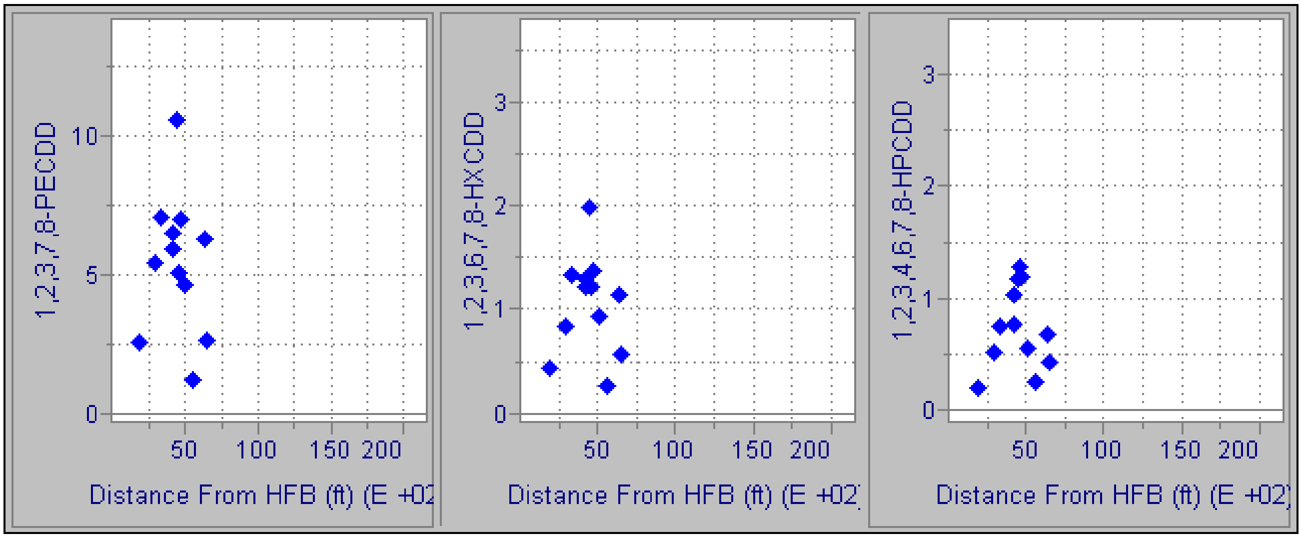

Figure 22. Congener response (selected dioxins, as TEQ) vs. distance from boiler for non-forested samples in ESE-SE direction

On the other hand, combining the non-forested samples in a wider swath, east to southeast (see Figure 23), demonstrates the same trend as shown earlier (for example, Figure 20).

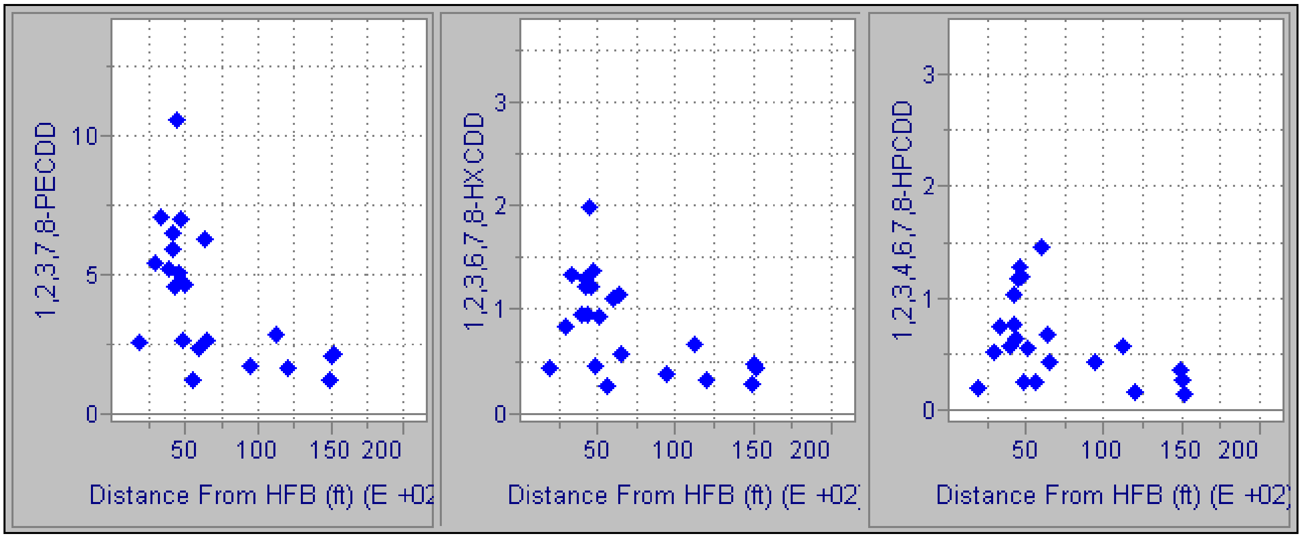

Figure 23. Congener response (selected dioxins, as TEQ) vs. distance from boiler for non-forested samples in E-SE direction

There are fewer sampling sites located in the southeast to south-southeast direction, but these few samples indicate a similar drop-off with distance, as shown in Figure 24.

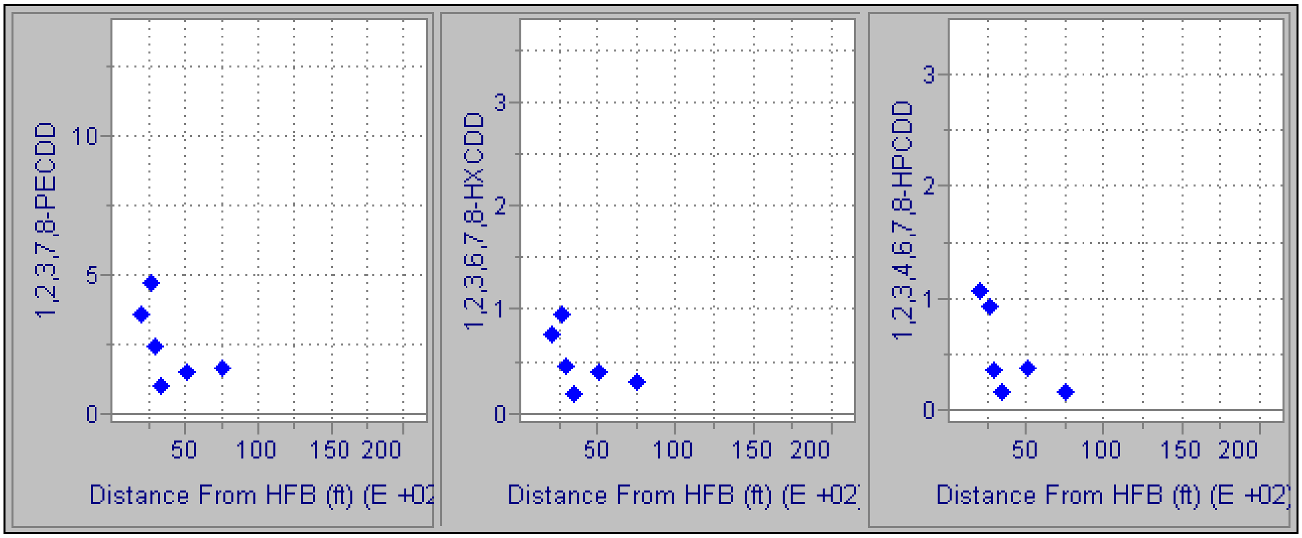

Figure 24. Congener response (selected dioxins, as TEQ) vs. distance from boiler for non-forested samples in SE-SSE direction

Spatial trends are not apparent for sampling sites in other directions.

6.2. MULTIVARIATE ANALYSES

Points at the extremes of the simplex formed in the ternary plot of the source amounts (see Figure 12) represent samples that most closely resemble potential source patterns. Extracting related information about each sample can help with understanding differences among samples and with determining the origin of the dioxin contamination.

In the source amounts plot shown in Figure 25, the points for the most extreme samples are highlighted (plotted points are filled); these are the samples most representative of each source (purest) and least affected by the other sources. Each group of highlighted samples will be investigated individually.

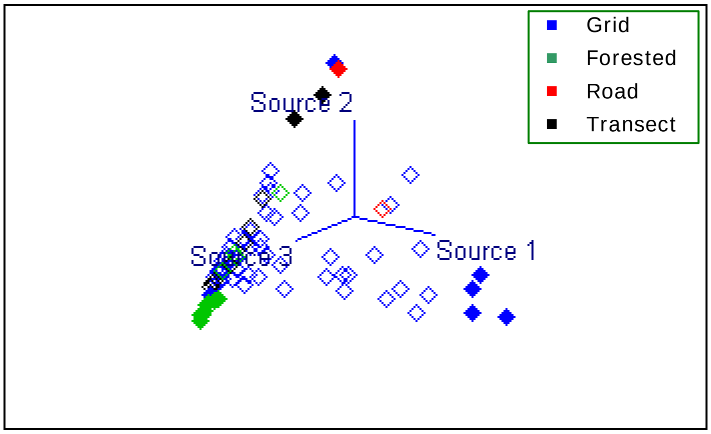

Figure 25. Ternary plot of estimated source amounts with samples representative of three sources highlighted

The normalized TEQ profiles corresponding to the highlighted samples on the Source 1 axis are shown in Figure 26. These profiles are unique in that the major contributor to the pattern is the 2,3,7,8-TCDD congener.

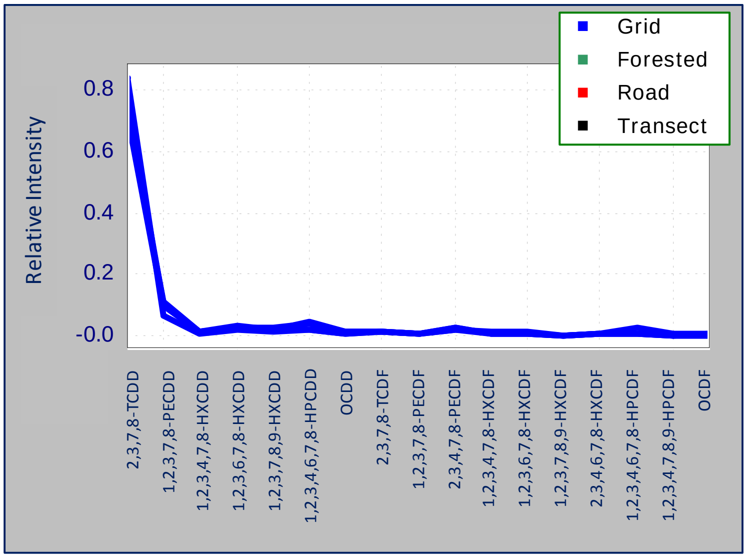

Figure 26. Source 1-related sample profiles

All but one of these samples were drawn from the West grid area, south and west of the boiler site, as shown in the pseudo map plot of Figure 27 (sampling locations shown as a function of X and Y coordinates).

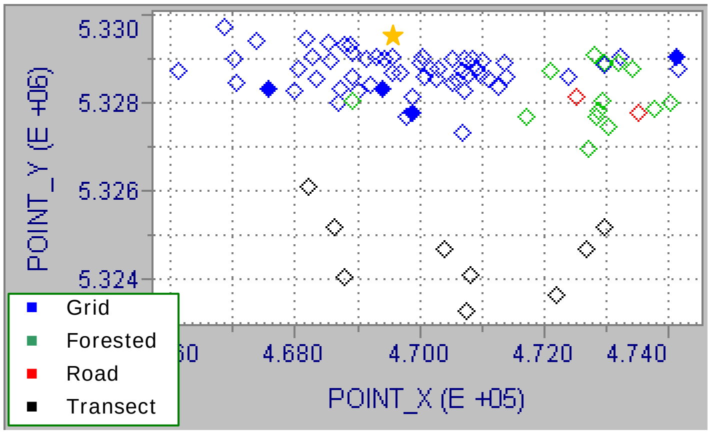

Figure 27. Source 1 sample site locations in geographic coordinates (orange star = HFB site)

The identifications for these samples are listed in Table 6.

Table 6. Source 1-related sample IDs

Index	Name
31	E499SS
65	W203SS
75	W213SS
76	W214SS

Profiles for the highlighted samples corresponding to the Source 2 pattern in Figure 25 are shown in Figure 28. The profiles are composed mostly of chlorinated dioxins: 1,2,3,7,8-PECDD, 1,2,3,6,7,8-HXCDD, 1,2,3,7,8,9-HXCDD, and 1,2,3,4,6,7,8-HPCDD.

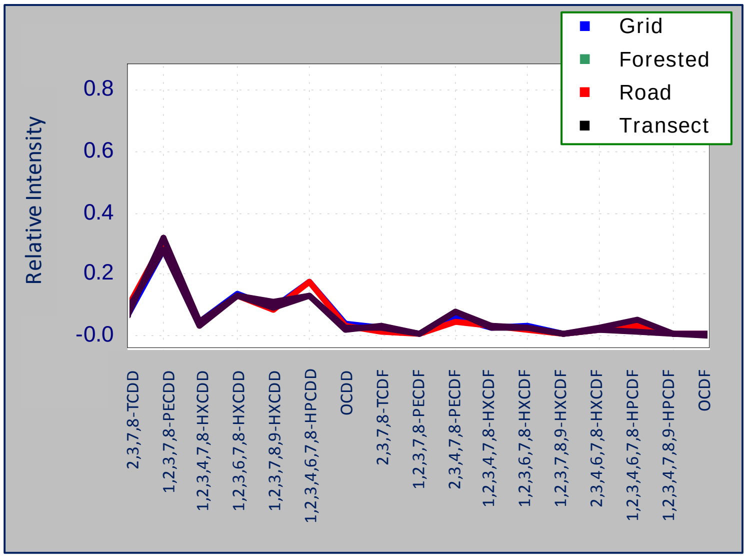

Figure 28. Source 2-related sample profiles

Locations of these samples are shown in the following pseudo map plot of Figure 29.

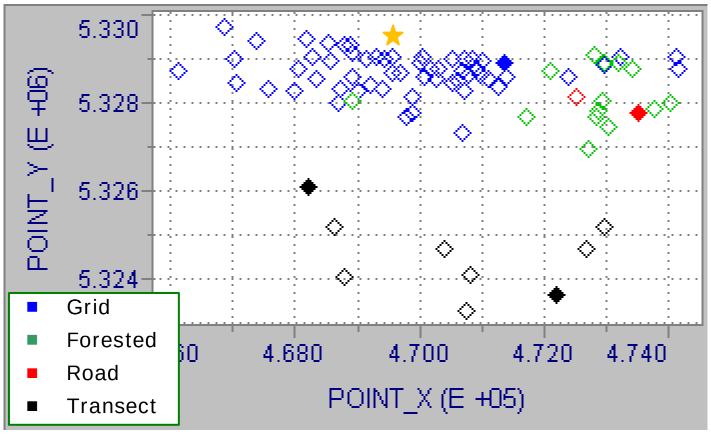

Figure 29. Source 2 sample site locations in geographic coordinates (orange star = HFB site)

Identifications of these samples are included in Table 7.

Table 7. Source 2-related sample IDs

Index	Name
24	E299SS
41	RD01SS
45	T104SS
51	T303SS

These samples were obtained from three disparate locations: next to the highway near the entrance to the city, in the uphill transect area, and in the East grid.

Figure 30 exhibits a selection of sample profiles corresponding to highlighted samples similar to the Source 3 pattern in Figure 25. Although these profiles have a nominal resemblance to those from Source 2, there is a larger contribution from the chlorinated furans. The major compounds present include: 1,2,3,7,8-PECDD, 1,2,3,7,8,9-HXCDD, 2,3,7,8-TCDF, and 2,3,4,7,8-PECDF.

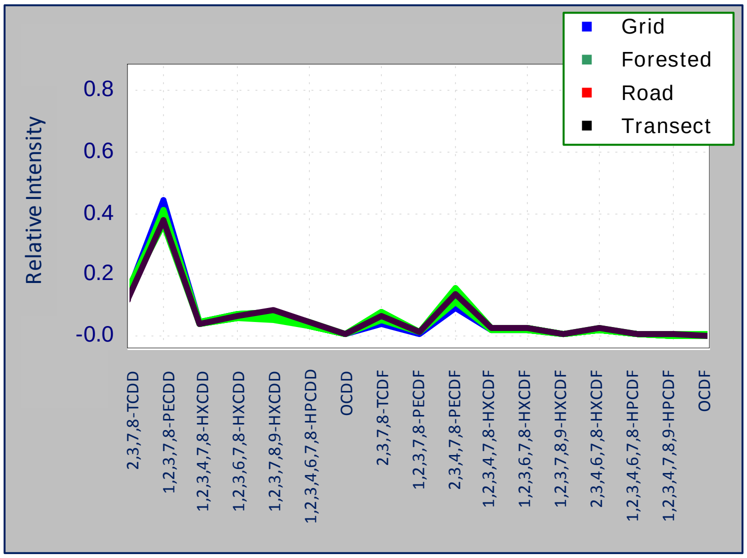

Figure 30. Source 3-related sample profiles

Of these more extreme Source 3-related samples, most are located in the forested sites in the East grid, as shown in Figure 31.

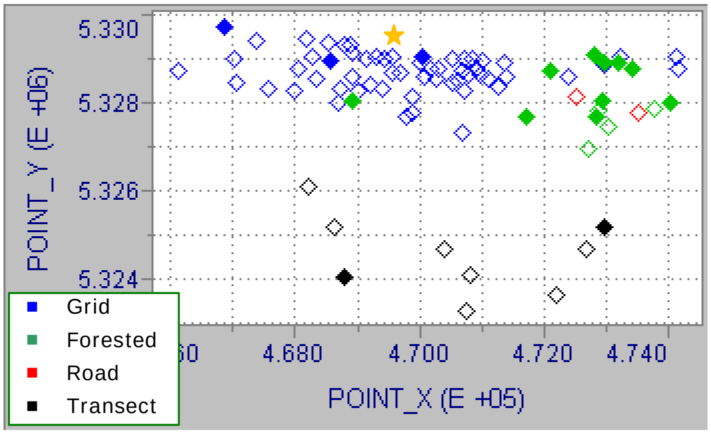

Figure 31. Source 3 sample site locations in geographic coordinates (orange star = HFB site)

Table 8 lists the identifications for the set of highlighted samples in Figure 31.

Table 8. Source 3-related sample IDs

Index	Name
13	E194SS
21	E206SS
33	FF02SS
34	FF03SS
35	FF04SS
36	FF05SS
37	FF06SS

38	FF07SS
39	FF08SS
40	FF09SS
44	T103SS
49	T301SS
66	W204SS
79	W299SS
80	W301SS

As shown in Figure 25, most of the samples lie in the direction of the Source 3 pattern, or at least fall along a line between Sources 2 and 3. Of the 83 samples in the working data subset, 64 (77%) have contributions of at least 40% from the Source 3 pattern (these points are highlighted in Figure 32); a few of these have similar contribution from Source 2.

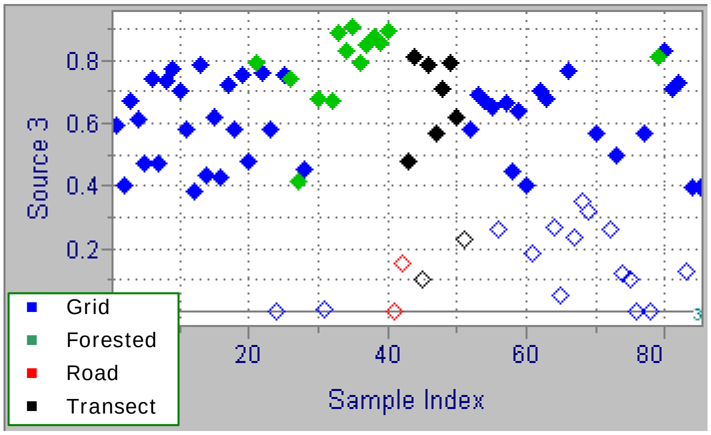

Figure 32. Samples showing at least a 40% contribution from Source 3

The profiles corresponding to the highlighted points in Figure 32 (see Figure 33), are, as expected, a blend of the two sources (2 and 3).

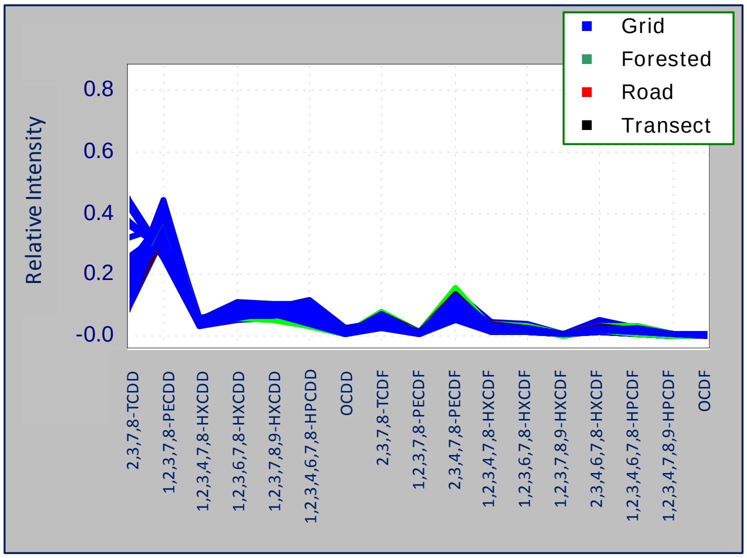

Figure 33. Profiles for samples with at least 40% Source 3

These samples are located throughout the study area, both west and east of the hog fuel boiler, as well as in the forested areas and upslope transects (see Figure 34).

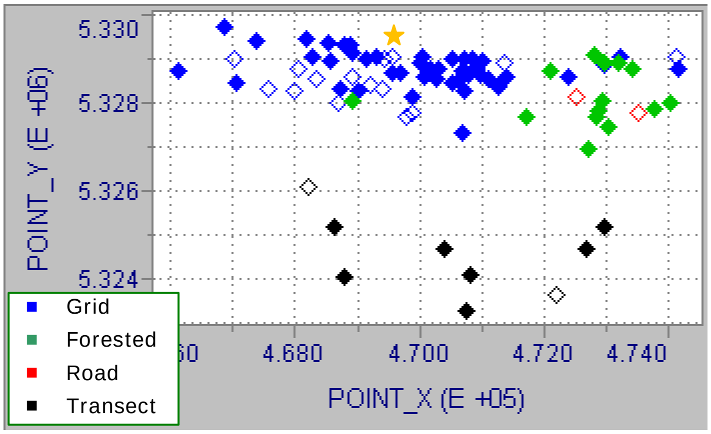

Figure 34. Geographical location of samples shown in Figure 33 (orange star = HFB site)

The patterns of dioxin and furan TEQ congeners are largely consistent throughout the study area—a substantial influence of the Source 3 pattern is demonstrated over a large portion of the study area—with only a few locations exhibiting notable differences.

6.3. COMMENTS ON INDIVIDUAL SAMPLES

Only two samples east of Lees Creek show profiles similar to the Source 1 pattern; both (E405SS and E499SS) were indicated to have had char present during sample collection. Other samples with char had profiles intermediate between Sources 2 and 3; two of these are of forest type (E402SS and E403SS). One of these forested samples (E403SS) had the highest TEQ of all samples (excluding the two outliers).

Most samples similar to the Source 1 pattern are found in the West grid; three are in the East grid (E103SS, E122SS, E197SS), as shown in Figure 35.

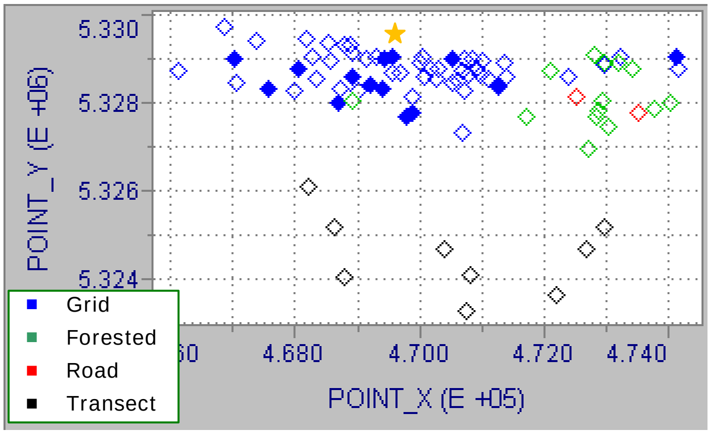

Figure 35. Geographical distribution of samples with large (>0.4) Source 1 contribution (orange star = HFB site)

Source 1 samples also tend to have TEQ values slightly higher than average, as shown in Figure 36.

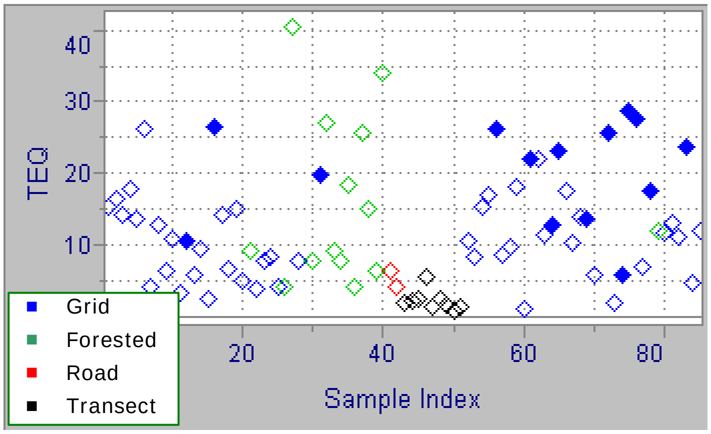

Figure 36. TEQ values relatively high for samples of large Source 1 contribution (highlighted)

Samples with relatively high proportions of patterns related to that of Source 2, though not ubiquitous, are encountered in all areas of the basin, as shown in Figure 37.

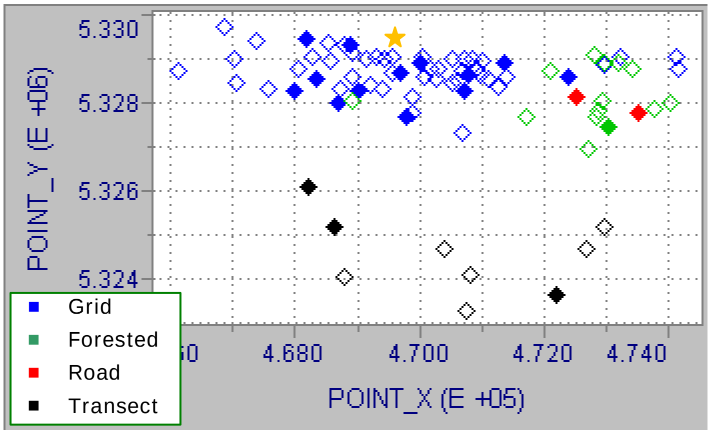

Figure 37. Geographical distribution of samples with large (>0.4) Source 2 contribution (orange star = HFB site)

As shown in Figure 38, these samples tend to have relatively lower TEQ values.

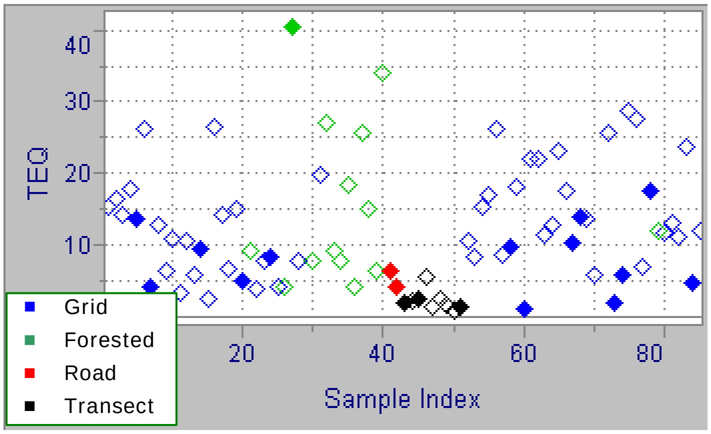

Figure 38. Relatively low TEQ values for samples of large Source 2 contribution

Samples with relatively high contributions from the Source 3 pattern are found throughout the basin with the exception of the west grid; only about half of those samples are thus characterized (see Figure 39).

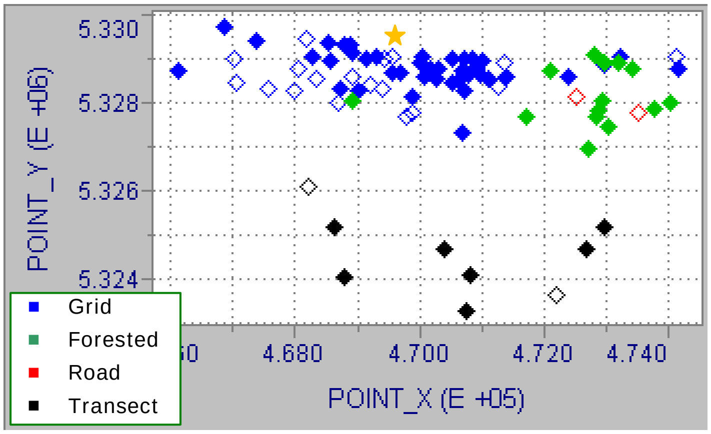

Figure 39. Geographical distribution of samples with large (>0.4) Source 3 contribution (orange star = HFB site)

These samples have TEQ levels that range from the lowest to the highest in the study (see Figure 40).

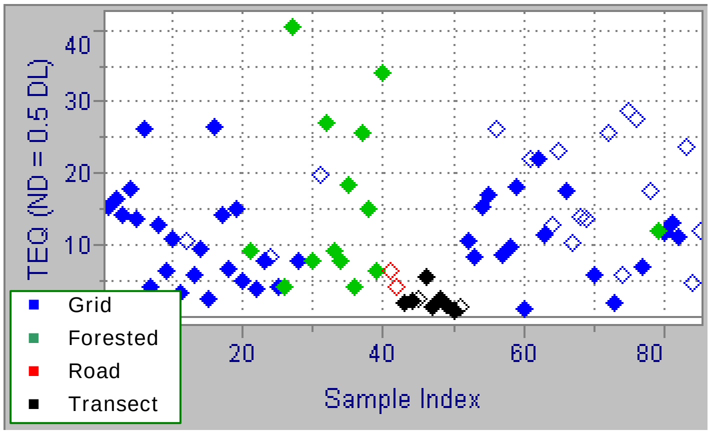

Figure 40. Widespread TEQ values for samples of large Source 3 contribution

All but one sample in the East grid closest to the boiler have relatively higher Source 3 contributions (see Figure 41). The single anomalous sample, located at the top of the ternary plot, has a profile more like that of a Source 2 pattern.

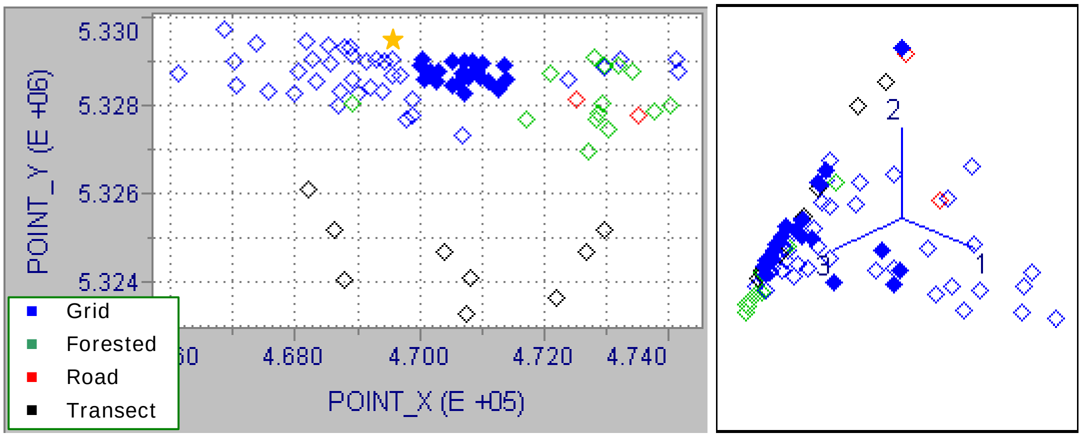

Figure 41. Nearest East grid samples show predominance of Source 3 contributions (orange star = HFB site)

Transect samples appear to fall on a line between Sources 2 and 3 (see Figure 42), but all have very low overall TEQ values. Two transect samples (T104SS and T303SS) have relatively elevated 1,2,3,6,7,8-HXCDD and 1,2,3,4,6,7,8-HPCDD but reduced 1,2,3,7,8-PECDD.

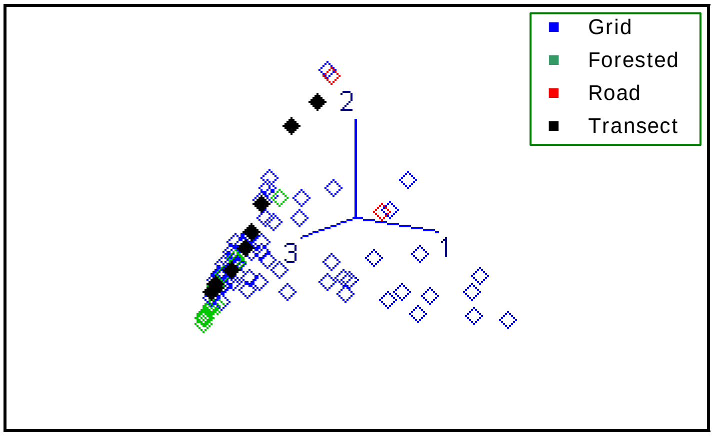

Figure 42. Source allocation of transect (upslope) samples

Two samples are dominated by contributions from a Source 2 pattern (the two sample points at the top of the ternary diagram in Figure 42). One is a road sample (RD01SS); the other is a grid sample (E299SS) that lies just east of Lees Creek.

Sample W196SS is near Olympic Memorial Hospital and is the West grid sample most like the Source 2 pattern but exhibits a very low TEQ (1.13). Samples W103SS and W198SS are also in the vicinity of the hospital but have profiles more like a Source 3 pattern with higher TEQ. If effluent from the hospital was deposited in the area and was a significant source, sites nearby would be expected to exhibit similar patterns. Because patterns at these two nearby sites resemble the Source 3 patterns found elsewhere, the medical waste incinerator must be a minor source.

Sample FF07SS is the site nearest to the Drennan-Ford Crematorium, lying just east of Lees Creek. Its profile is similar to those of the other forested samples in the East grid.

Although two samples were excluded as outliers, they can be compared with the other samples by predicting the source amounts with the ALS model. In the ternary plot shown in Figure 43, sample W209SS (taken adjacent to Peabody Creek and a major intersection uphill to ONP; this sample had an extreme TEQ) appears as an extreme example of a Source 1 pattern, while E406SS (taken from Island View Drive) appears as an extreme example of a Source 3 pattern.

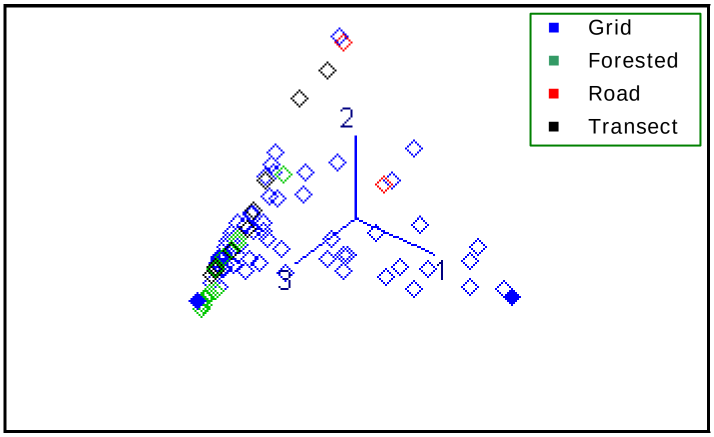

Figure 43. Projections of the two outliers (blue, highlighted points) in the space of source contributions

However, these two samples do not fit the ALS model perfectly as shown by their residuals, shown as thicker lines in Figure 44.

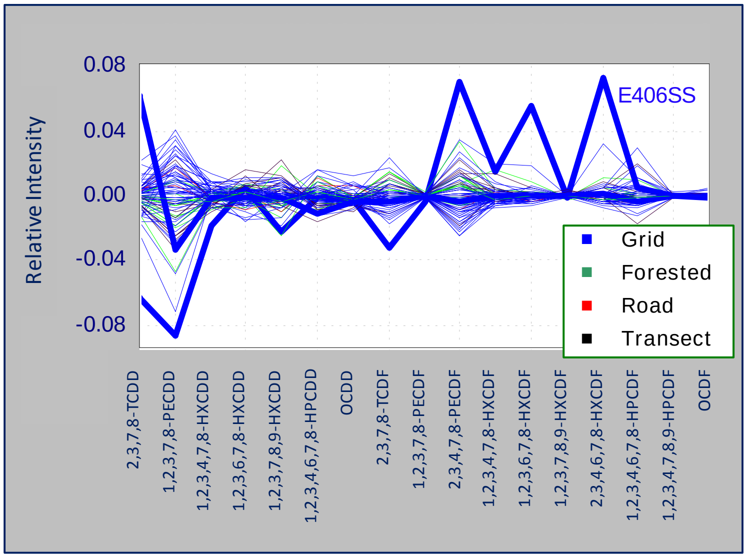

Figure 44. ALS model residuals following prediction on all study samples

These outliers are different because there is likely another source contributing to their composite patterns. The deviations in the shapes of their residuals are a clue to what congeners might be present in another source. We already saw that sample W209SS is unusual by the extremely high amount of 2,3,7,8-TCDD (see Figure 2). The residuals for sample E406SS imply there may be a substantial amount of unmodeled chlorinated furans.

6.4. COMPARISONS WITH OTHER PROFILES

Published literature was searched for studies in which dioxin congener patterns were evaluated and in which the congener values were available. Of the hundreds of citations obtained, data from the most relevant groupings were extracted. These included urban (and some rural) soil surveys, United States Environmental Protection Agency's (U.S. EPA's) inventory of air emission sources, chemical manufacture and incidental dioxin occurrence in chemical products, and a special search for emissions data for hog fuel boilers burning salt-laden wood. We also compiled available information on other soil dioxin measurements in Port Angeles. The corresponding tables of congener data were extracted and put into a format from which comparisons could be made to the Study data. Table 9 lists these sources.

Many of the comparison patterns were extracted from publications on dioxins in the scientific literature. Others were obtained from public documents concerning dioxin studies. The last category of patterns came from personal communication with other researchers in the field. These data have not been published.

Table 9. Sources of comparison patterns

Material Description	Data Source
Seattle region urban sediments	Windward Environmental, LLC 2010
Denver urban soils	U.S. EPA, Region 8 2001
Spokane urban storm drains	Lubliner 2009
U.S. rural soils	U.S. EPA 2007
U.S. typical soils (urban, rural)	U.S. EPA 2000
Australia urban soils	Muller et al. 2004
Norway urban soils	Andersson and Ottesen 2007; Andersson 2009
British Columbia (Canada) soils	Van Oostdam and Ward 1995
Mt. Pleasant landfill (WA) area soils	Ecology & Environment 1999
Port Angeles (WA) graving dock soils	Landau Associates, Inc. 2003
Tse-whit-zen (Port Angeles) soils	Environment International Government Ltd 2009; Beckley 2009
Rayonier RI soils (on- and off-property)	Integral Consulting, Inc. 2007; Ecology & Environment, Inc., 1998b (ESI)
U.S. EPA inventory, dioxin air emissions sources	U.S. EPA 2006
U.S. EPA dioxins in chemicals	U.S. EPA 2000; Burkhard and Lukasewycz 2008; Jiang et al. 1997
Rayonier HFB stack test	Foster Wheeler Environmental Corporation 1997
Canadian HFB stack tests	DeAbreu 2009; Glass 2009; Luthe and Prahacs 1993
Rayonier ash samples	Foster Wheeler Environmental Corporation 1997; Ecology & Environment, Inc., 1998a and 1999

Many of the comparison profiles bear no resemblance to the proposed source profiles observed in the Study. Several strategies were used to contrast the Study site and comparison profiles, then to reduce the comparison set to those most likely to be of relevance in characterizing the Study patterns.

6.4.1. PCA ANALYSIS

The combined Study and comparison data were first analyzed by principal components analysis (PCA) to get an idea of the diverse nature of the profiles. In a PCA scores plot, samples that are similar will plot in proximity to one another while samples that are dissimilar will plot separated. In Figure 45, the plotted points are colored by their origin.

Many sample groups can be observed in this plot, although there is a rather compact group near the center. The Study samples are highlighted with the filled diamonds. They appear to fall into two regimes: those in the lower left have higher contributions from Source 1 while those nearest the center have major contributions from Sources 2 and 3.

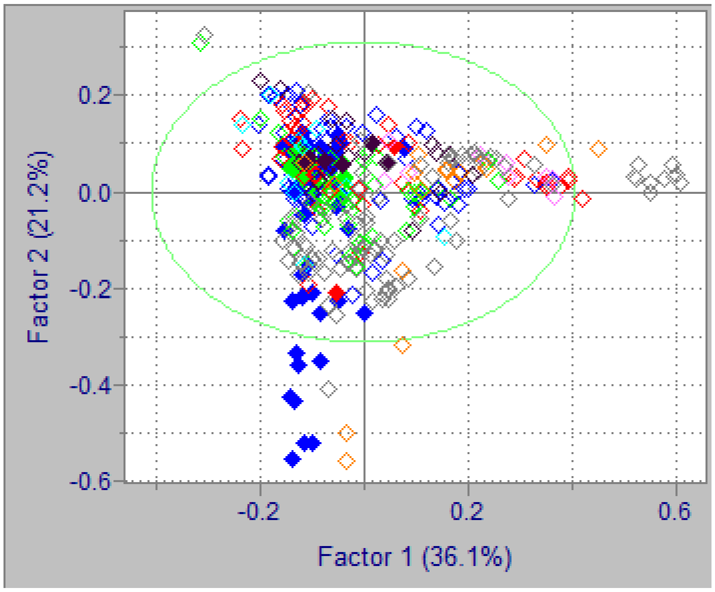

Figure 45. Scores from PCA of combined Study and comparsion data sets

By highlighting and showing only the predominantly Source 3-related Study samples (see Figure 46), we can see that they are tightly clustered, indicating their similarity, especially with respect to the comparison profiles. This plot includes the single stack test from the hog fuel boiler with the Source 3-related samples for comparison.

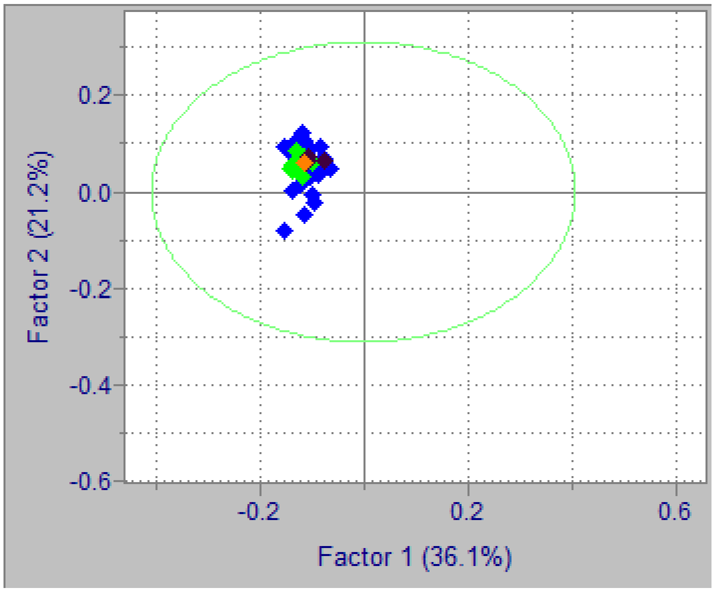

Figure 46. PCA scores of Source 3-related samples and stack test sample

Each type of comparison pattern was highlighted at the same time as the Source 3-related samples to visually discover which were similar based on the concept of proximity. For example, samples known to contain PCP are seen to be quite dissimilar from Source 3-related samples, as shown in Figure 47.

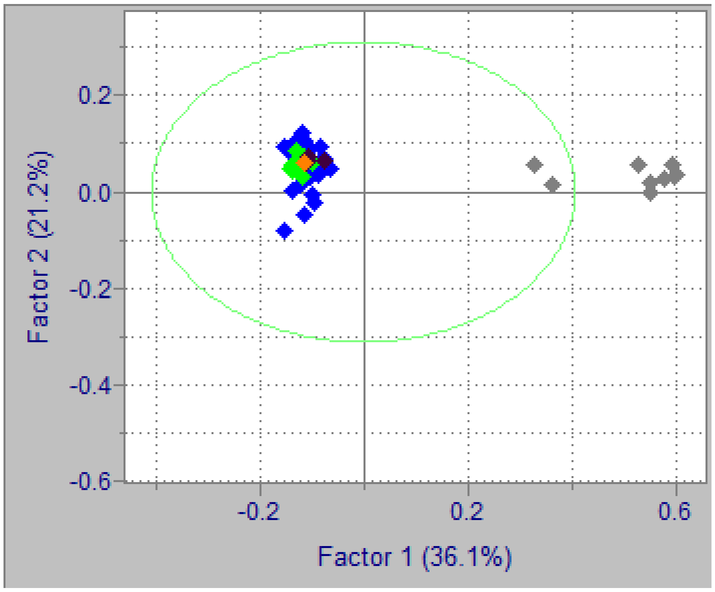

Figure 47. Scores of Source 3-related and PCP samples

On the other hand, samples from Canadian hog fuel boilers tend to overlap with the Source 3-related samples as shown Figure 48. No other type of pattern in our collection was found to overlay the Source 3-related samples.

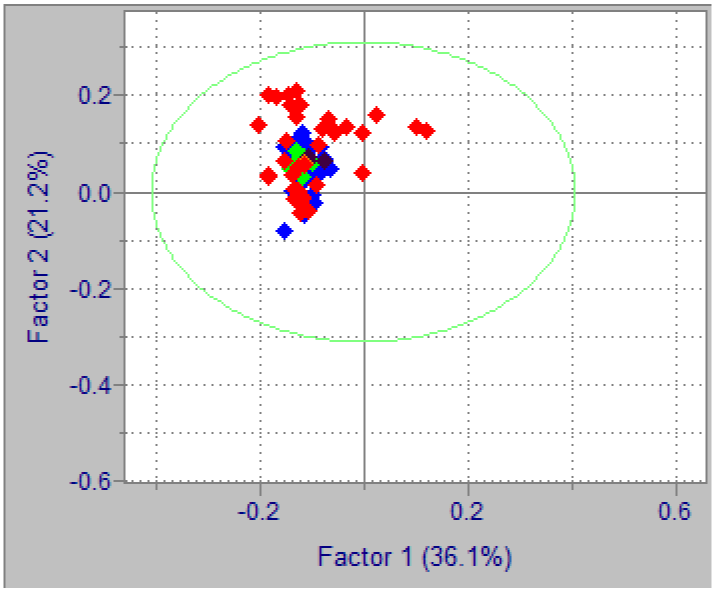

Figure 48. Scores of Source 3 and Canadian HFB samples

6.4.2. CORRELATIONS TO SOURCE PROFILES

Correlation coefficients were calculated between each comparison profile and each proposed source pattern from the ALS results. Table 10 lists the best matches to each source, in decreasing order of match value.

Table 10. Correlations of comparison profiles

Correlation to Source 1		Correlation to Source 2		Correlation to Source 3	
Comparison Profile	**Corr.**	**Comparison Profile**	**Corr.**	**Comparison Profile**	**Corr.**
DenvRes NW R-10	1.00	PA-soils SL20	0.99	CANST59	0.99
DenvRes NW R-11	0.99	PA-soils ECO26	0.97	CANST26	0.99
EPAinvy Tire Combust	0.97	PA-soils SL21	0.97	CANST44	0.99
DenvRes NW R-3	0.94	SpokSeds Superior	0.96	PA-soils JNR01	0.99
		CANST57	0.96	PA-Ash LF-01-08SB	0.99
		CANST48	0.95	PAash F-Ash-89	0.98
		TseWZ J9YR6	0.95	CANST7	0.98
		PA-Ash RS-18-SS	0.95	PA-Ash LF-01-04SB	0.98
		CANST51	0.95	PA-soils ECO22	0.98
		SpokSeds Union	0.95	PA-soils ECO29	0.98
		DenvRes SW R-11	0.95	PA-soils ECO28	0.98
		CANST10	0.94	PA-soils ECO32	0.98
		CANST49	0.94	CANST45	0.98
		PA-soils ECO30	0.94	CANST55	0.98
		PA-soils ECO33	0.94	PA-soils ECO20	0.98
		CANST56	0.93	CANST42	0.98
		Chem SSMED-2DL	0.93	PA-soils ZMR02	0.98
		PAash F-Ash-93	0.93	CANST36	0.98
				PA-Ash RS-12-SS	0.98
				CANST1	0.98

Source 1 appears related to patterns from residential soils as well as from tire combustion. Among the comparison profiles, Source 3 was most similar only to other analyses of Port Angeles soils and to samples obtained near Canadian hog fuel boilers. Source 2 presents a slightly mixed story, having similarity to some urban sources as well as to a few of the Canadian hog fuel boiler samples. It is likely a composite of these two types of patterns.

6.4.3. CLUSTER ANALYSIS SIMILARITIES

The set of comparison profiles was analyzed using Hierarchical Cluster Analysis (HCA) with the incremental linkage method. Many of the comparison profiles cluster into groups of more than one or two similar patterns. From the dendrogram view of these results, it is possible to select representative profiles for each cluster, thereby reducing the redundancy in the set to the most representative profiles. Figure 49 illustrates this filtering approach.

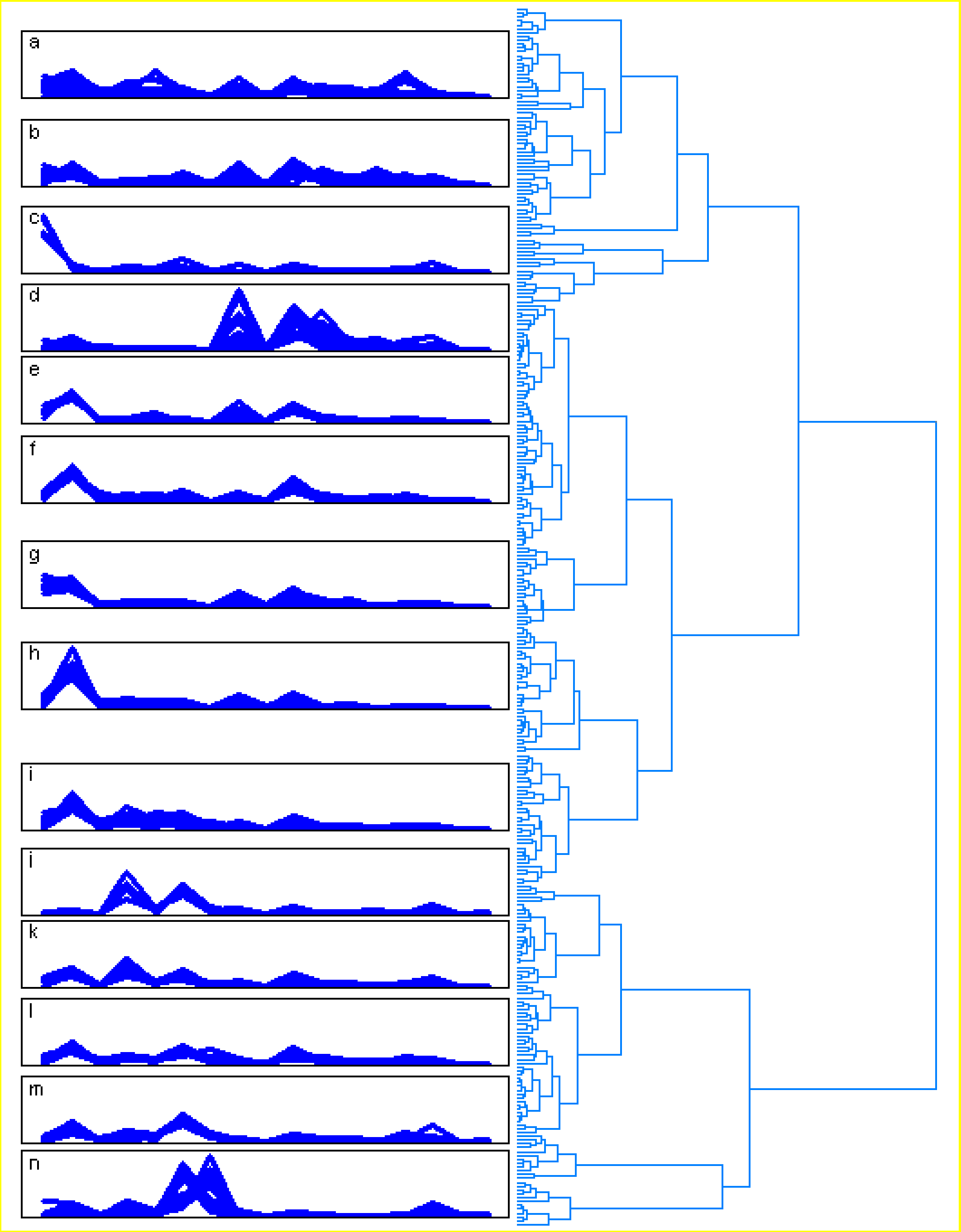

Figure 49. Cluster analysis of comparison profiles

Profile sets e and h in the above figure bear some resemblance to Source 3 (see Figure 30), while some of the samples in groups f and i resemble Source 2. Finally, Source 1 is similar only to samples in group c. None of the other groups appear to be closely related to the Study samples.

Unrelated profiles were removed and representative patterns from each cluster were retained for further analyses. Because of the similarities among samples within a cluster, it was not necessary to retain redundant patterns.

6.4.4. MIXTURE ANALYSIS OF COMBINED STUDY AND COMPARISON PROFILES

The set of comparison profiles was merged into the Study data set, and the ALS algorithm was run on the combined data. The number of sources sought by the algorithm was increased because the additional variability introduced by the comparison profiles would clearly indicate many more sources. The relative uniqueness of many of the comparison sources was quite clear, however, and their contributions to the Study profiles were negligible. In fact, this is a good indication that the profiles with low contributions are not related to the Study patterns and can, therefore, be discarded from further consideration.

For example, in Figure 50, sample contributions shown in the subplot of Source 2 vs Source 5 are significant because the contribution amounts are high.

On the other hand, the subplot for Source 1 versus Source 4 (outlined in red) shows that almost all samples are clustered near the origin, indicating that sources 1 and 4 do not contribute to these samples. Comparison profiles related to extracted sources that contribute less than 20% to the Study samples were removed from further consideration.

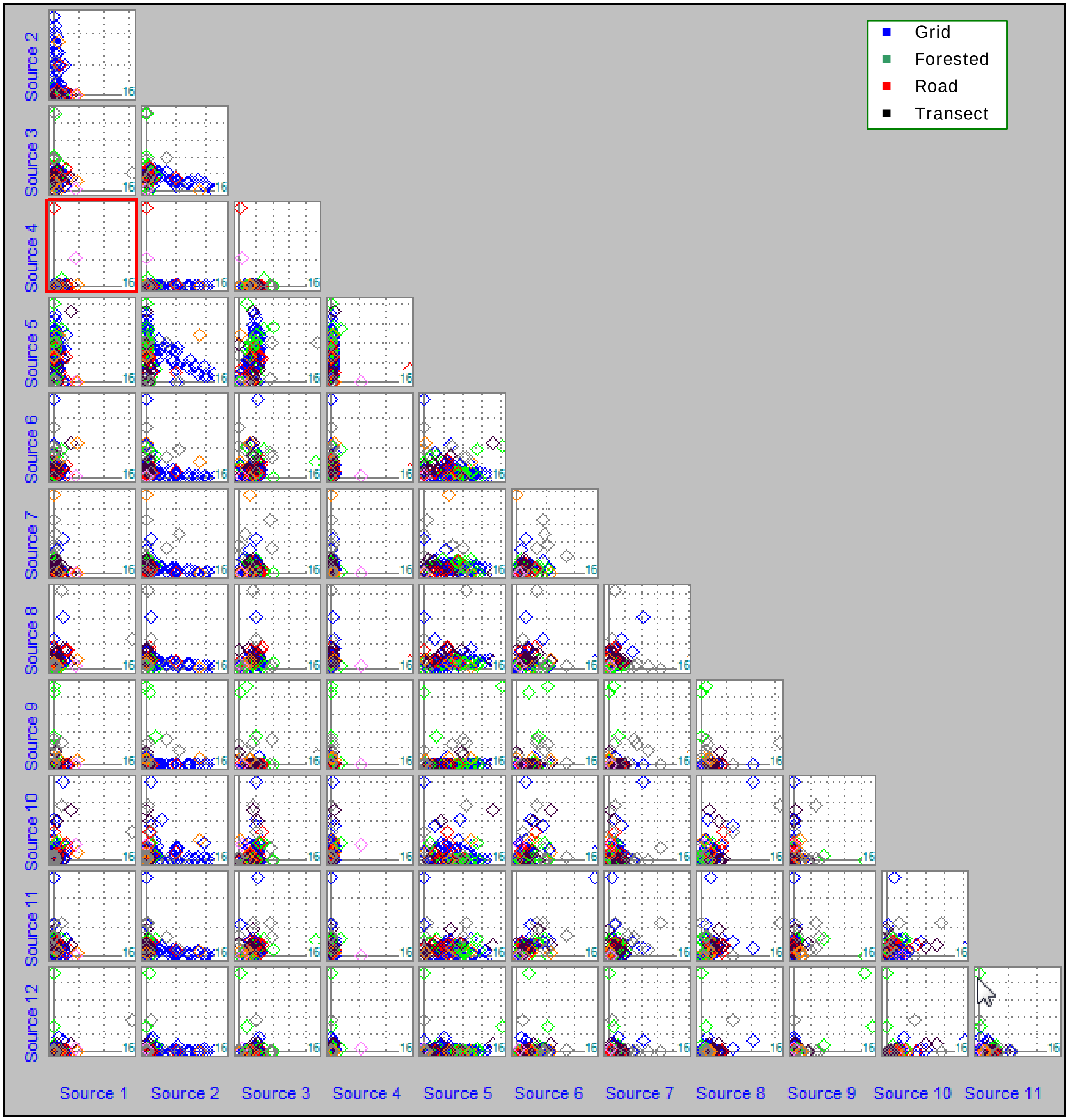

Figure 50. Source contributions from ALS analysis (using 16 sources) of Study plus comparison patterns

The set of comparison patterns was filtered to remove those patterns demonstrated to have no relevance to the Study, as described above. From the remaining sets of comparison patterns, representative profiles were selected by two directed methods to reduce the number of patterns from each set, simplifying subsequent interpretation. First, the Kennard and Stone sample selection procedure was applied to each category of material in the comparison sets, with specification to retain the three most representative samples. Second, a PCA was run on each category, and the sample nearest the centroid of the set was also retained. Because there was some overlap between the two procedures when the category contained only a few samples, only three patterns were retained for some comparison profile types. The result of these procedures produced a reduced set of 47 comparison patterns segregated into the categories identified in Table 11.

Table 11. Final set of comparison patterns

Category	Number
Port Angeles ash	3
Port Angeles graving dock	3
Tse-whit-zen soil	6
Port Angeles soil	7
Canada hog fuel boilers, 4 sites	17
Canada NPRI	3
Rural soils	3
EPA inventory	5

This reduced set of comparison patterns was merged with the study data, and ALS was performed on the combined data. With a six-source ALS model, the source contributions indicate that two of the comparison source patterns contribute very little to the Study samples. They were removed and the mixture analysis was repeated.

Subsequent ALS analysis of the Study data combined with the refined comparison set required only four sources, and the contribution of each source pattern to the Study samples is significant. That is, the comparison patterns in the refined set are relevant. The following figures highlight those samples for which the indicated source pattern is significant[5]. The profiles for the important comparison patterns are shown together with the Study profiles.

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[5] Sources revealed when running ALS on different combinations of data sets may result in source ID numbers that are not the same among the different analyses. This is the case in this analysis where the IDs for Sources 2 and 3 are in a different order than in the main study.

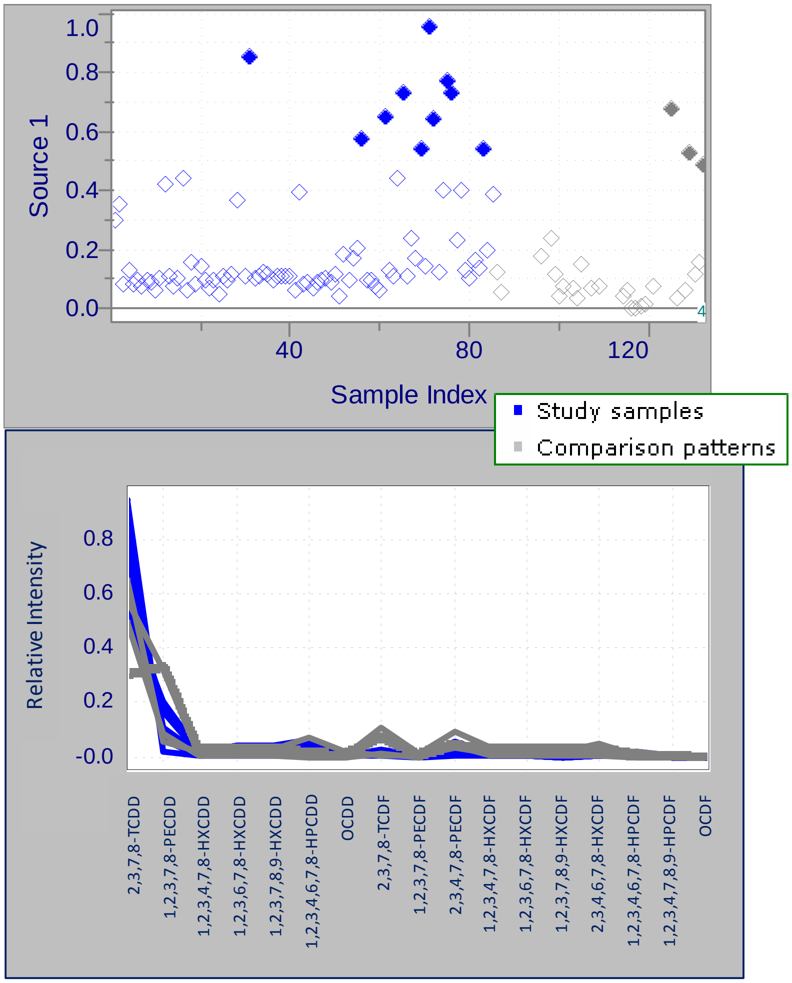

Figure 51. Source 1 contributions to combined set of Study and comparison samples

As in the ALS analysis of only the Study samples, Source 1 is dominated by a single congener, 2,3,7,8-TCDD. Comparison patterns found to exhibit a similar shape were of certain residential soils and from one example of tire combustion[6]. In these comparison patterns, 1,2,3,7,8-PCDD also appears; in addition, there is a small contribution from the lower-chlorinated furans. As mentioned earlier, all but one of the Study sites with high contribution from Source 1 are located west and south of the boiler site.

In this ALS analysis of the combined patterns, Source 2 is a major contributor to the bulk of the Study samples, responsible for 50% or more of the composition for 63 samples (73% of the Study samples). This is similar to the result for analysis of just the Study samples (see Figure 32). The patterns seen in these Study samples (see Figure 52) are similar to those from prior analyses of soils in the Port Angeles area.

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[6] There may be other patterns that resemble source 1--for example, 2,4,5-T is known to be dominated by the 2,3,7,8-TCDD isomer--but the complete 17-congener set was not available during the time of the study.

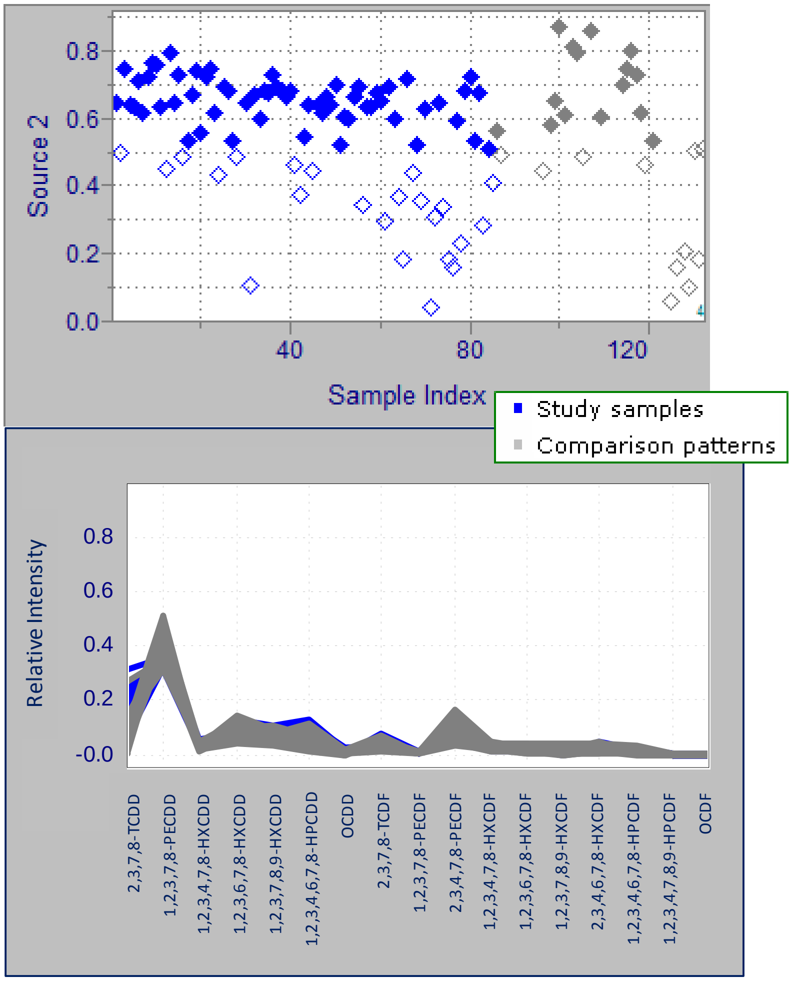


Figure 52. Source 2 contributions to combined set of Study and comparison samples

In addition, many of the samples described in studies on Canadian hog fuel boilers exhibit patterns similar to that of Source 2. Of all of the industrial examples of dioxins/furans found in a review of the literature, only these Canadian studies were found to share patterns with those at the Port Angeles site.

As shown in Figure 53, the pattern of Source 3 is similar to that of Source 2, but the relative intensity of chlorinated furans is lower. Only four of the study samples had a contribution of more than 40% from this source, and these sample sites were in four different sub-regions of the study area. In the earlier analysis of only the Study samples (see Figure 29), these same four samples were the only ones found to share this pattern.

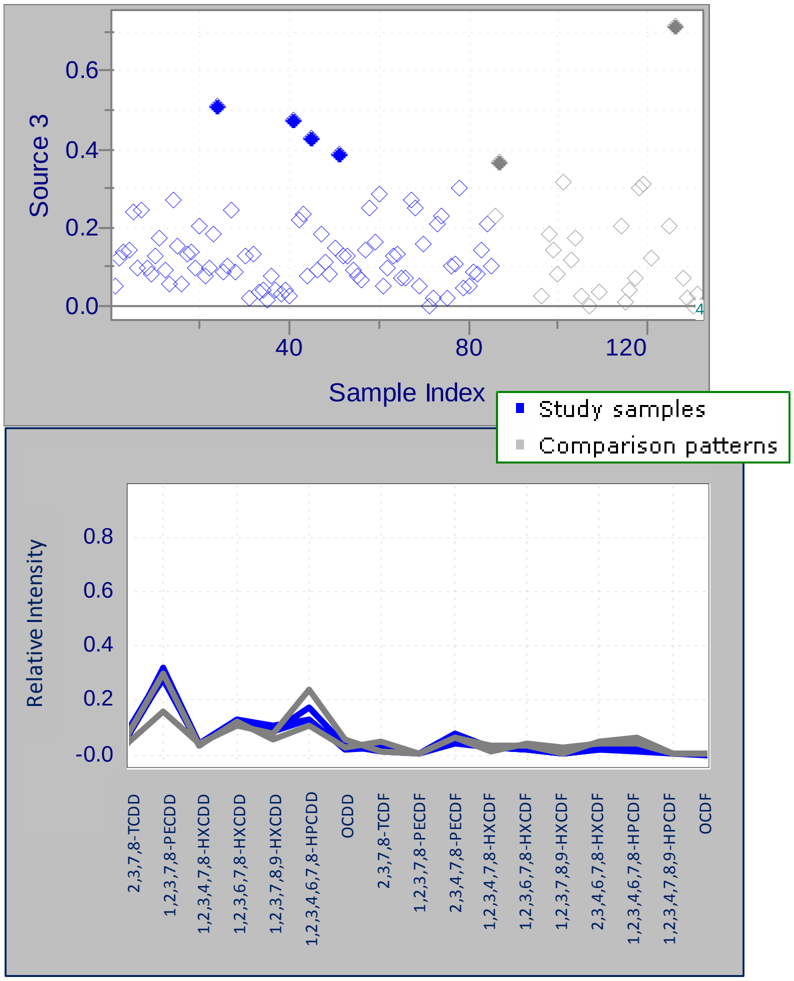


Figure 53. Source 3 contributions to combined set of Study and comparison samples

In the set of comparison profiles, only a Port Angeles ash and a single urban soil (Spokane) showed a pattern similar to that of Source 3.

In the final proposed source profile (Figure 54), the intensity of 1,2,3,7,8-PCDD relative to the two lower-chlorinated furans is lower than in the other sources. Only two Study samples have a contribution from Source 4 greater than 30%. This is in agreement with the analysis of only Study samples shown earlier. Among the comparison patterns, a Canadian hog fuel boiler sample, Tse-whit-zen soils, a auto gasoline sample, and a municipal waste sample were relevant.

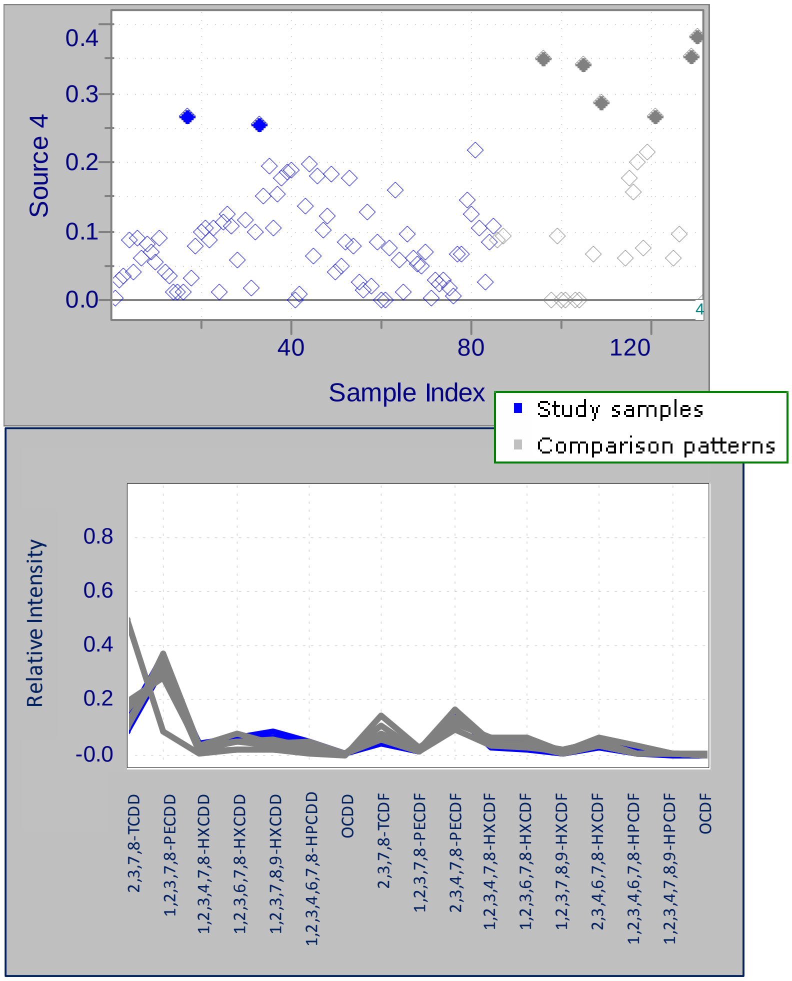


Figure 54. Source 4 contributions to combined set of Study and comparison samples

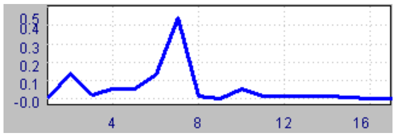
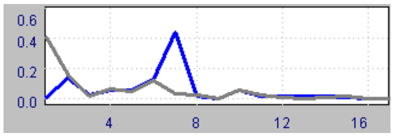
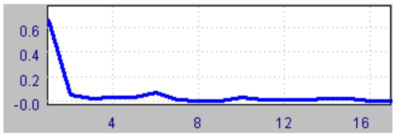
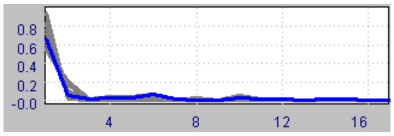
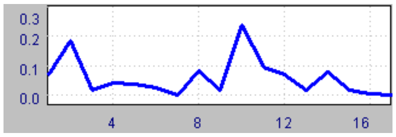
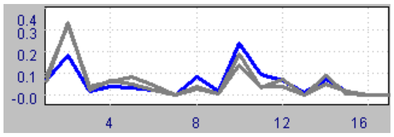
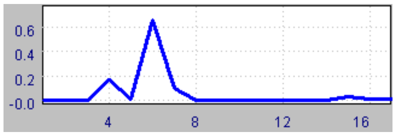
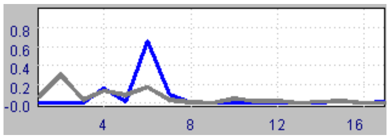
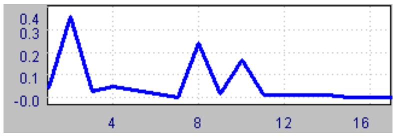
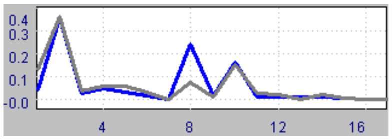
The two patterns from the U.S. EPA inventory, a municipal waste combustion sample and a gasoline combustion sample, exhibit similar intensities in the penta isomers of dioxins and furans; however, the relative intensity of the 2,3,7,8-TCDF is higher, leading to a less-than-perfect match. Nevertheless, because these types of combustion sources are present in the Port Angeles area, they could be contributors to the character of soils in the region.

6.4.5. TARGET TESTING

Based on the evaluations of contributing and non-contributing congener profiles from the comparison data, patterns were chosen as candidate sources to the Study data. Included in this set of patterns (see Table 12) were those of commonly identified dioxin sources. To test whether these candidate patterns were possible contributors to the Study data, ALS was run in target mode. In the first pass, only the candidate profiles were included in the ALS computations. Afterwards, all Study profiles were compared to this ALS model. This approach is similar to FALCON (U.S. EPA 2004), developed by the U.S. EPA for source matching with known source patterns.

In Table 12, candidate patterns are shown together with the pattern of the most similar Study profile. In addition, the quality of the match is shown as a correlation coefficient. The candidate patterns shown here were those retained after the filtering steps mentioned earlier. Patterns from the source inventories that were removed from consideration would also have low match values.

Table 12. Candidate source patterns and closest matching profiles from Study set

Candidate	Candidate profile	Best Study match	R^2
Aust 4 (Urban soil)			0.20
DenvRes NW R-10 (Residential soil)			0.99
EPAinvy MWC (Municipal waste combustion)			0.58
Chem PCP-Na-3 (Penta-chlorophenol)			0.01
HFB (Hog fuel boiler stack test)			0.76

The residential soil source has a clear relationship to some samples in the Study set with a very high correlation coefficient (0.99); several other samples have correlations that are higher than 0.95. Generally, a correlation of 0.95 or greater is considered a very good match.

Some of the forested samples had a correlation with the Rayonier hog fuel boiler stack test of around 0.76. Because the relative ratios of the 2,3,7,8-TCDF and 2,3,4,7,8-PECDF peaks are different by a factor of 2, the overall match quality is degraded, however, as can be seen in the table, there is very good agreement for the remaining congeners.

Two samples had a 0.58 correlation with the municipal waste combustion source, a value too low to be considered a good match.

None of the other candidate sources matched the Study samples to a degree that would suggest they should be considered sources for the patterns seen in the Study. Apart from residential soils, the typical materials in the U.S. EPA inventory would not be implicated as sources for the patterns in the Port Angeles study.

6.5. CONTOUR MAPS

A complementary way to look at the congener patterns as a function of location in the Port Angeles basin is to compare each proposed source profile contribution in a contour map.

In the following figures, the contributions of each of the three proposed source patterns are plotted as contour maps, where the magnitude of a source contribution is proportional to contours of greater darkness. Areas in the plot with little color show where there is little contribution from a source. Each sampling location is represented on the plots by an open circle, and the location of the hog fuel boiler is denoted by a yellow hexagon. Values between points are computed by linear interpolation such that areas without sampling events are inferred by estimation from existing data.

The transect samples are not shown in the contour maps because their overall TEQ values are much lower than those of samples from the main grid and because their distances from the other samples would make estimating contour values unrealistic. The two road samples are also excluded, so that the maps show only those sites designated as grid or as forest samples.

Because Source 1 appears to be related to patterns in residential soils, such a pattern could be expected to be present in much of the basin. The contour map for Source 1 shows highest contributions on the southern edge of the city. It is probable that, in the other parts of the city, the contributions of other source types have masked the influence of the Source 1 pattern.

As shown earlier, only four samples have major contributions from Source 2; two of these samples show as "hot spots" on the contour map for Source 2. One of the "hot spots" is the easternmost roadside sample. This pattern is a minor contributor to much of the basin.

The major contributor to the patterns observed in the majority of the sample locations was that of Source 3. The corresponding contour map shows that highest levels occur mostly in the more easterly portion of the study region. Exceptions can be observed in the two unusual samples with high contributions from the Source 2 pattern.

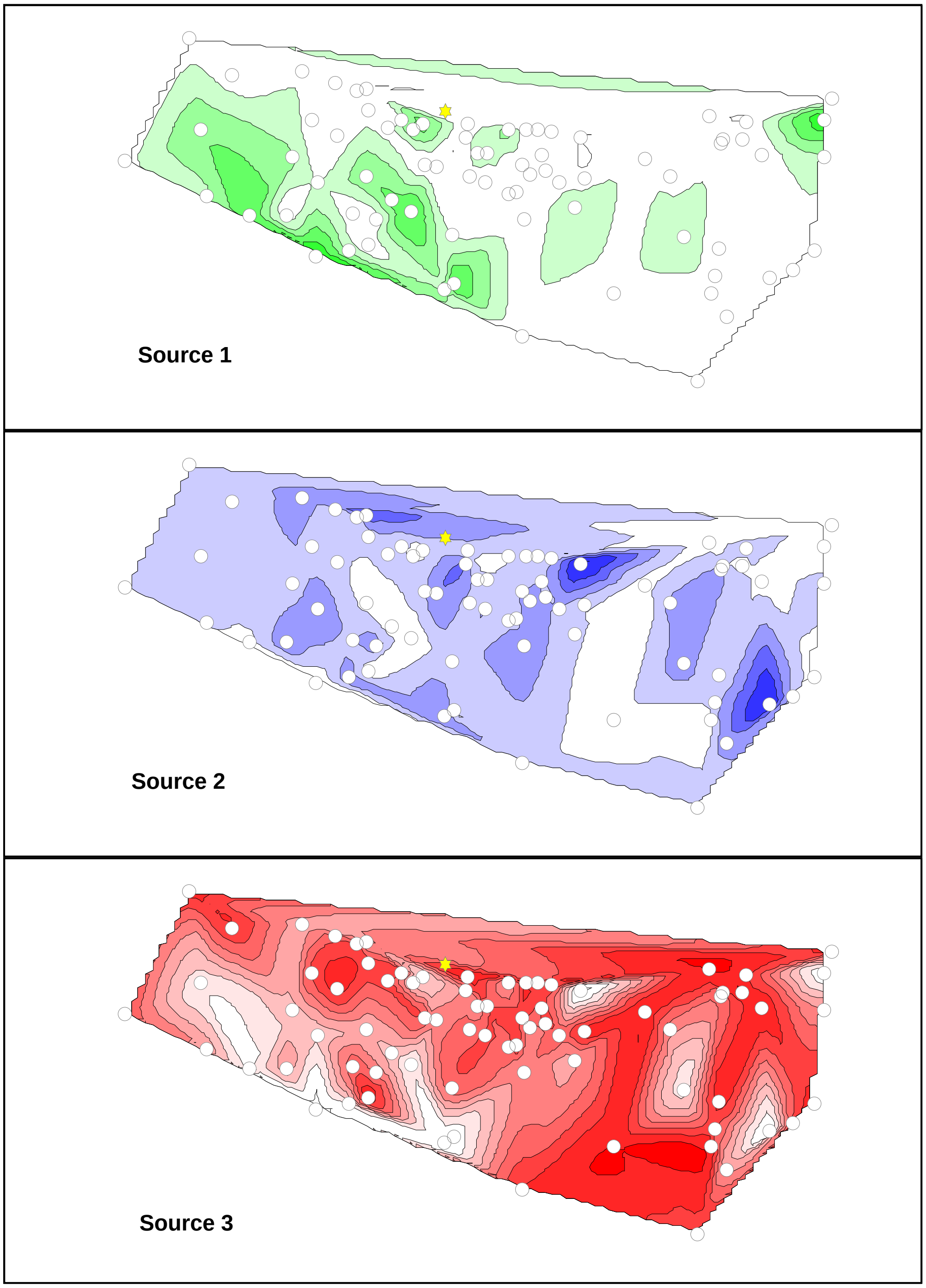


Figure 55. Source contribution contour maps for a 3-source ALS model

It is possible that the two unusual samples flagged as most representative of the Source 2 pattern are anomalous. One of these samples was collected adjacent to the major thoroughfare accessing the city (Highway 101) and would likely experience an impact by the large amount of auto and truck exhaust. If these patterns were excluded from the multivariate analysis, there could be an effect on the allocation of source profiles.

The mixture analysis was repeated with the two anomalous samples removed. In this analysis, over 99% of the variance can be explained with just two sources. The corresponding source profiles look very similar to those found in a three-source solution before removing the samples driving Source 2 (see Figure 56).

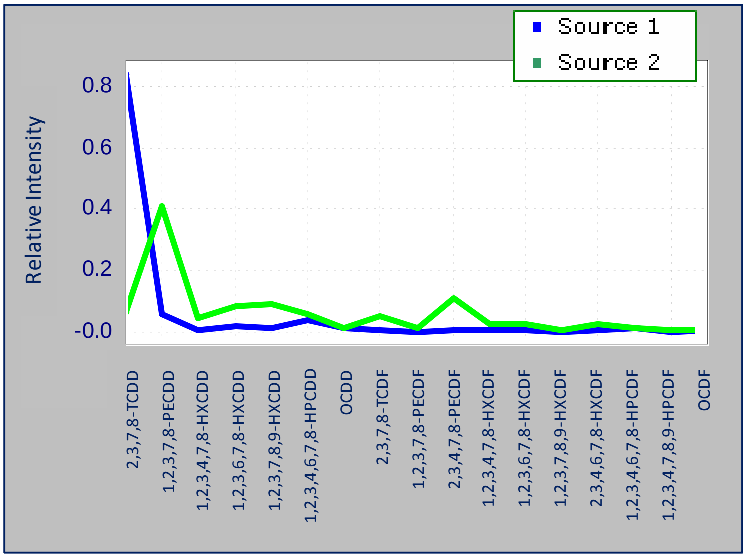


Figure 56. Source profiles for a 2-source solution

The first source (blue trace in the figure) is essentially identical to that found earlier, while the second source in this case looks like an amalgam of Sources 2 and 3 from the earlier analysis. This pattern (the green trace in the figure) shows a major contribution from the 1,2,3,7,8-PCDD and nearly equal intensities for several chlorinated dioxins and furans. As shown in Figure 57, the bulk of the samples have the largest contributions from Source 2, thus Source 2 would be considered the major contributor.

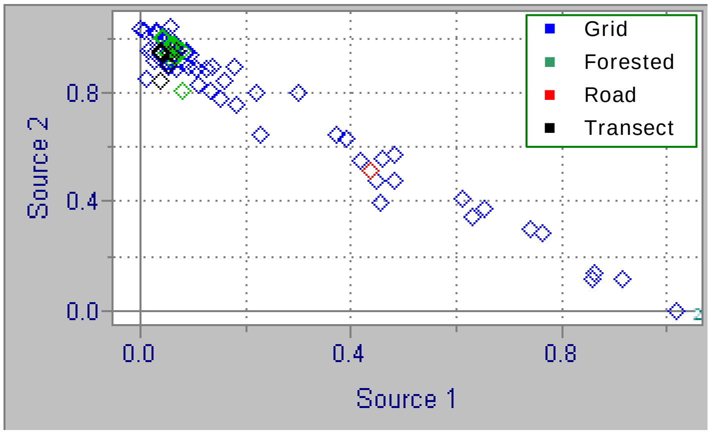


Figure 57. Source contributions to the Study samples, 2-source solution

Contour maps of the source contributions shown in Figure 57 help visualize these conclusions. As with the contour maps shown earlier, the contributions of each of the two proposed source patterns to the grid and forested samples are plotted as contour maps (see Figure 58), where the magnitude of a source contribution is proportional to contours of greater darkness.

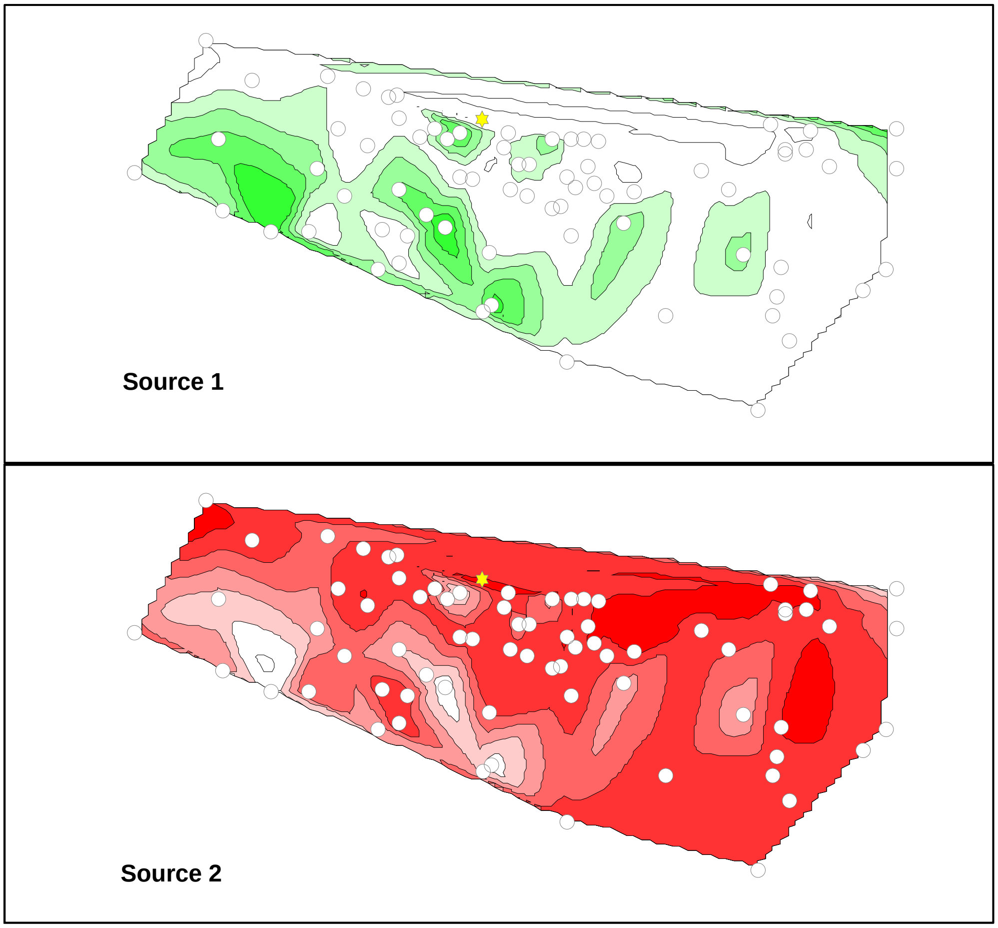


Figure 58. Source contribution contour maps for a 2-source ALS model

As before, sites in the more rural, southern part of the city exhibit profiles consistent with residential soils while the majority of samples exhibit the signature of the second source.

7. SUMMARY

Table 13 lists the important data evaluations undertaken as part of this study, including the different data sets that were processed.

Table 13. Data processing stages

Data Set	Treatment	Discussion
Rayonier Soils Study Data		
Congeners, raw data	PCA, ALS	Results dominated by OCDD; outliers apparent and excluded
Congeners, variance scale[1]	PCA, ALS	4 or 5 sources apparent; scale method inflates sample of lowest intensity, skewing results; otherwise, similar to TEF scaled data
Congeners, TEF scale	**PCA, ALS**	**3 or 4 sources apparent; no effects of scaling; method chosen for all subsequent analyses**
Total homologs	PCA, ALS	3 or 4 sources apparent; results similar to TEF scaled data
Comparison Data		
Canadian HFB mills	HCA, ALS	HFB profiles show basic pattern but vary in relative intensity of dioxins vs furans
U.S. EPA inventory of sources	HCA, ALS	Wide variation in patterns of congeners with majority unrelated to patterns seen in Study
Urban soils	HCA, ALS	There is no universal urban soil; patterns vary as function of location and local chemistry
Port Angeles soils, ash	HCA, ALS	Patterns from different studies show overall similarity, across years, by location in region and type of material
Comparison superset	HCA, ALS	Combined all comparison data into a single superset to facilitate data combinations (below)
Combined Data		
Study + Comparison superset	HCA, ALS	Majority of comparison samples are unrelated to Study data and are discarded for next steps
Study + Common profiles	HCA, ALS	Matching to "common" sources (wood burning, municipal incineration, cars and fuels) shows many types irrelevant to Study data
Study + Relevant profiles[2]	HCA, ALS	Retain patterns of greatest similarity to Study data from the two previous combinations
Study + Selected profiles[3]	HCA, PCA, ALS	Retain patterns of greatest similarity to Study data from the three previous combinations

Notes:

[1] Also evaluated was scaling by range (not shown); results were similar to those from variance scaling.

[2] Patterns selected which contribute at least 20% to sample composition.

[3] Selection was done in two steps for each comparison subset. Method of Kennard & Stone applied, requesting 3 samples, followed by PCA analysis, using Mahalanobis distance to identify sample nearest centroid.

The most informative results were found using mixture analysis on the Study data and on the Study data combined with the refined set of comparison profiles. Each analysis suggests that the Port Angeles samples can be apportioned into three sources, two of which show interesting contributions from the tetra-, penta- and hexa-chloro dioxin and furan congeners. Additionally, when the Study data were combined with the comparison profiles, a fourth pattern was considered plausible. This pattern is similar to two of the other three proposed source patterns.

Source 1 is dominated by 2,3,7,8-TCDD and is the major contributor in about 10 of the study samples. Based on patterns of dioxins found in residential soils in other studies, it is likely that dioxins in these samples were of a similar nature.

Sources 2 and 3 show, overall, a similar pattern of dioxin and furan congeners. They can be characterized by their relative intensities, as shown below.

- A pattern in which the 1,2,3,7,8-PCDD is only slightly more intense than the 1,2,3,6,7,8-HxCDD and 1,2,3,4,6,7,8-HpCDD, and the furans are depressed (see Figure 59).

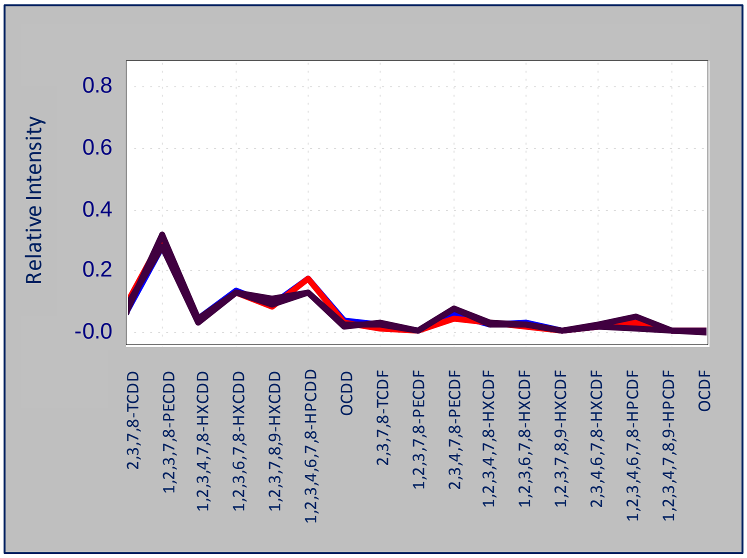


Figure 59. Example Study profiles similar to the pattern of Source 2

- A pattern in which the 1,2,3,7,8-PCDD is the major component, and in which there are mostly equal amounts of 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 2,3,6,7-TCDF, and 2,3,4,7,8-PCDF (see Figure 60).

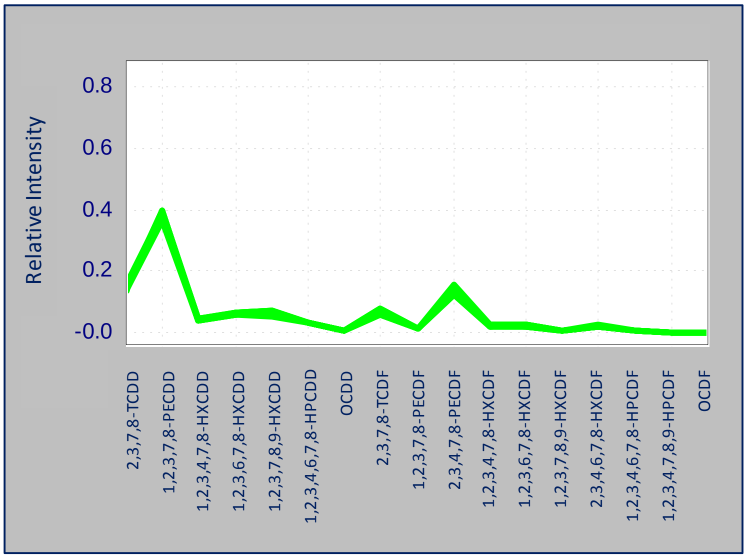


Figure 60. Example Study profiles similar to the pattern of Source 3

This latter pattern is characteristic of the majority of samples in the Study. Similar profiles were found in samples analyzed in other studies of the Port Angeles basin as well as in studies of hog fuel boilers in western Canada.

In addition, samples that exhibit this pattern are found in all regions studied within the basin, at low and high TEQ levels. At the same time, because the samples that exhibit the profiles noted in Source 2 are also found in locations dispersed in the basin, it is likely that their patterns were modified by contributions from other, minor sources. Likely candidates are contributions from residential wood combustion (fireplaces, burn barrels, etc.) and from gasoline combustion, primarily from automobiles and diesel-burning trucks.

Finally, the contour plots help to illustrate the observation that the pattern of chlorinated dioxin and furan congeners is ubiquitous in the areas in eastern Port Angeles and is common in other in-town areas as well. The contribution of this pattern to areas further from the city is diminished, giving way to a more typical congener pattern reflecting residential soils.

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D DIOXIN/FURAN SOURCE PROFILES

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Dioxin/Furan Source Profiles

An inventory of chemical patterns for multiple dioxin/furan sources is presented graphically in this appendix. The data sources used to compile this inventory of dioxin/furan profiles are listed as references below and are identified for each source. Not every potential source for dioxins/furans is included here, but most of the major sources are represented.

The toxicity of dioxins/furans is evaluated based on 17 2,3,7,8-substituted congeners, which are a small subset of the total number of congeners. Source profiles presented here reflect those 17 2,3,7,8-substituted congeners. For each source, two profiles are presented: one based on bulk congener concentrations (blue), and a second one based on calculated TEQ values (red).[22] The set of TEF values used to scale bulk congener concentrations has changed over time. All of the TEQ profiles presented here were developed using the current set of TEFs (WHO-2005; Van den Berg et al. 2006) to calculate TEQs from original bulk concentrations. The TEQ profiles are thus presented on a consistent and equivalent basis.

Both the bulk profiles and the TEQ profiles are normalized (sum over 17 congeners equals 1) so that they reflect chemical patterns and not magnitudes. The Y-axis scale can be understood as fractional contribution to the total; the bar heights thus represent the fractional contributions of individual congeners, and the set of such contributions provides the source profile. (Note that the Y-axis scales vary across sources depending on the maximum congener contributions). The X-axis for all profiles lists the 17 2,3,7,8-substituted congeners in the same order. Dioxin/furan chemical profiles presented in this manner support visual comparisons both within and across sources.

Comparing the bulk (blue) and TEQ (red) profiles for individual sources shows that there are large shifts in the chemical profiles depending on which measure is used. TEF values range over more than 3 orders of magnitude and the rescaling of bulk concentrations by TEFs has a large impact on the profile shape.

Comparing the profiles of one type, either bulk or TEQ, across various sources shows that there are differences in the patterns from one source to another. These differences can be used as one factor in evaluating the likely contributions of various sources to measured dioxin/furan concentrations, for example in unmixing analyses.

The profiles shown here are representative of the listed sources, but variability in the profiles within a single source type should be recognized. One facility may have somewhat different

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[22] For all profile types except two, bulk congener concentrations were used as a starting point and then scaled using TEFs to develop TEQ profiles. The exceptions are the class of residential wood burning profiles and the asphalt plant profile, which were available only as TEQ profiles in EPA 2006 [reference 7 below]. Bulk congener values for those two types of profiles were derived from TEQ profiles [adjusted to reflect WHO 2005 TEFs] by dividing each congener TEQ value by its appropriate WHO 2005 TEF. Because the TEF-scaled values are given as 0 for most OCDF and some OCDD entries in the EPA 2006 profiles for residential wood burning, back calculations of bulk concentrations for those congeners in the residential wood burning profiles may be zero, which may be an artifact of the way in which TEQ profiles are reported in EPA 2006.

profiles over time, especially if there are changes in facility feedstocks, operations, or pollution controls. Different facilities within a source class are also expected to show some degree of variation in profiles. Laboratory analyses of typically low-concentration dioxins and furans also introduce variability in the results. In cases where multiple datasets are available for a single source type, variability in profiles has been demonstrated. Applications of dioxin/furan profiles like those compiled here should take such variability within source class into consideration.

This graphic inventory of dioxin/furan profiles illustrates that bulk and TEQ profiles can differ for a source and that sources have different profiles.

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BULK PROFILE **TEQ PROFILE**

Rayonier Hog Fuel Boiler - 1995(a)

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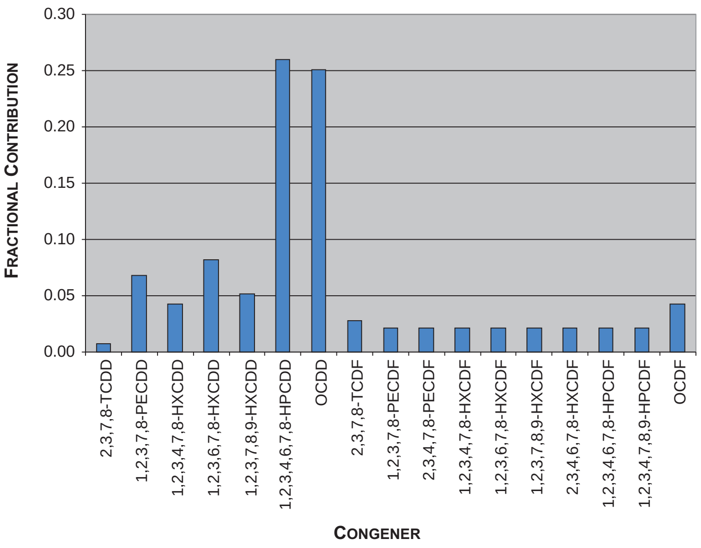

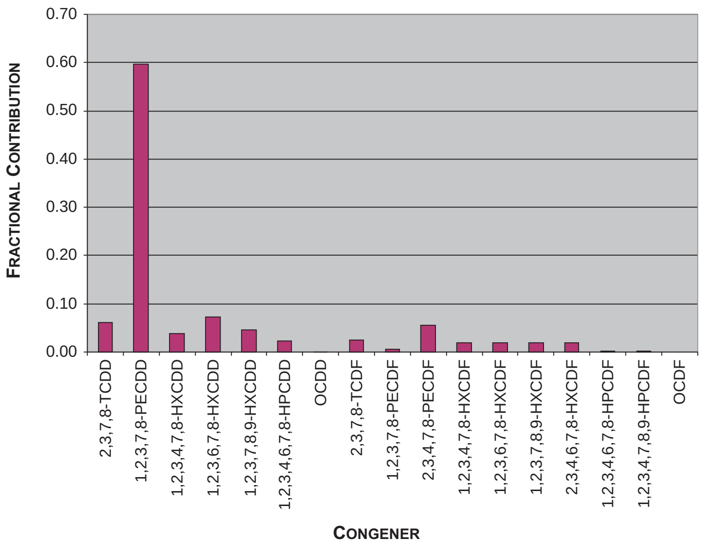

Rayonier Hog Fuel Boiler - 1995(b)

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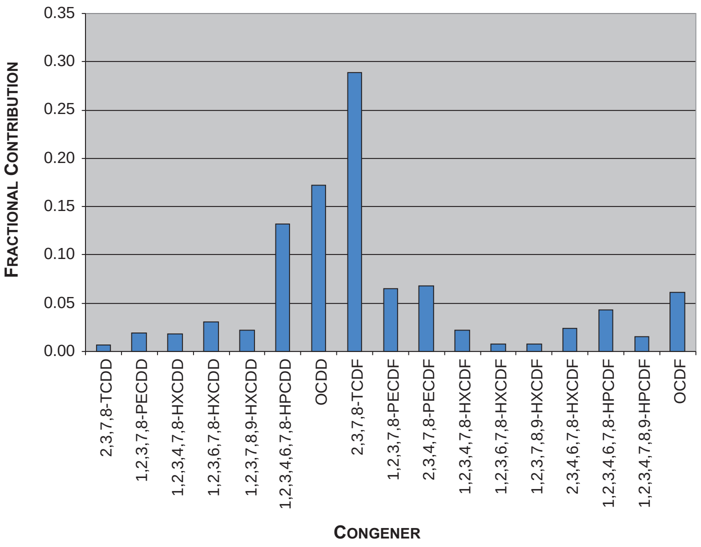

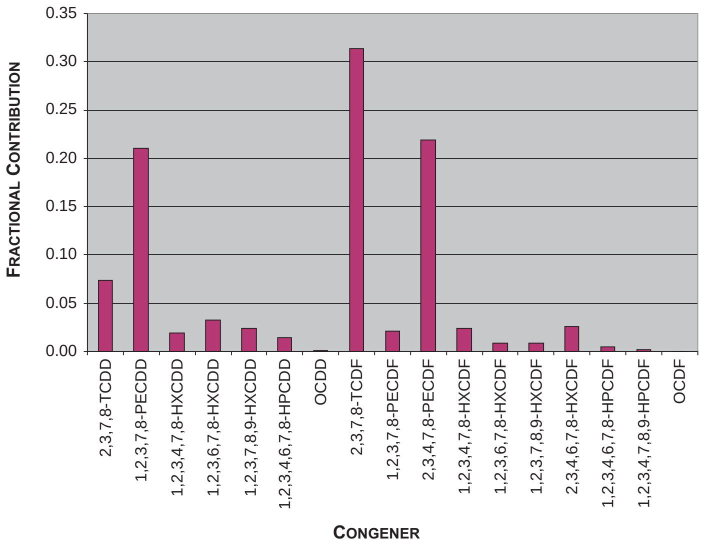

Rayonier Hog Fuel Boiler Ash - 1989

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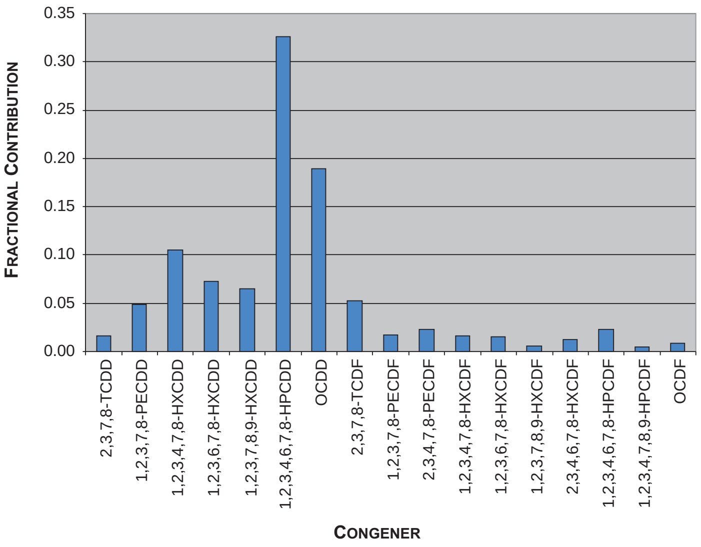

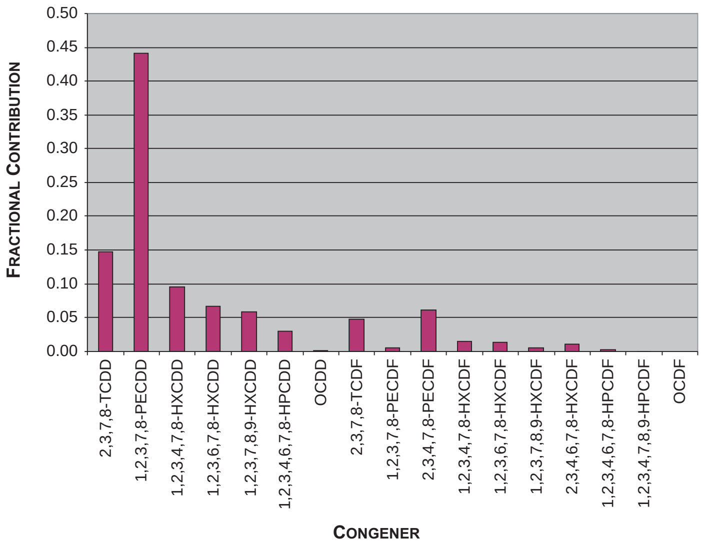

Nippon Hog Fuel Boiler - 2009

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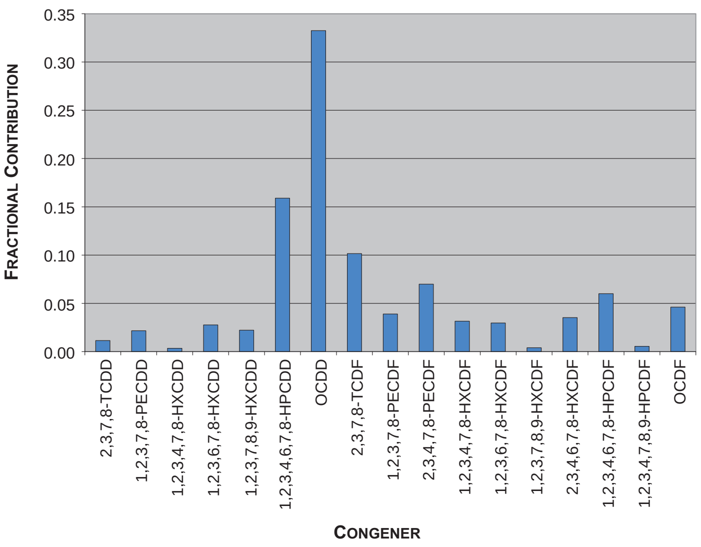

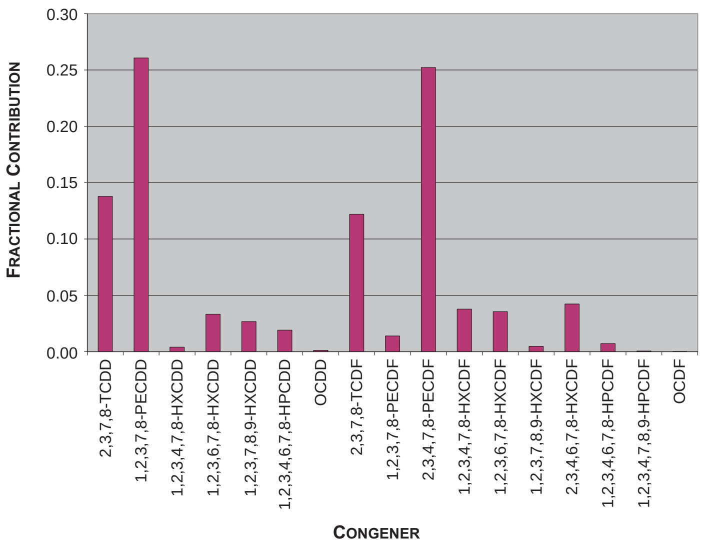

Canadian Hog Fuel Boiler 1 - 2007

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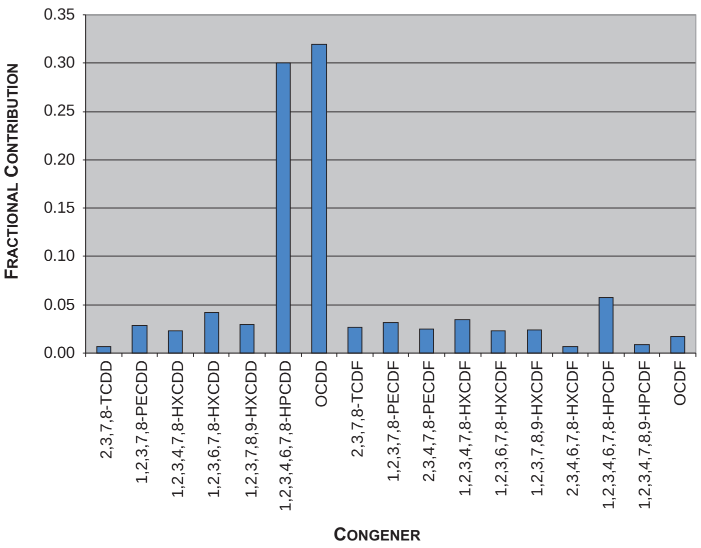

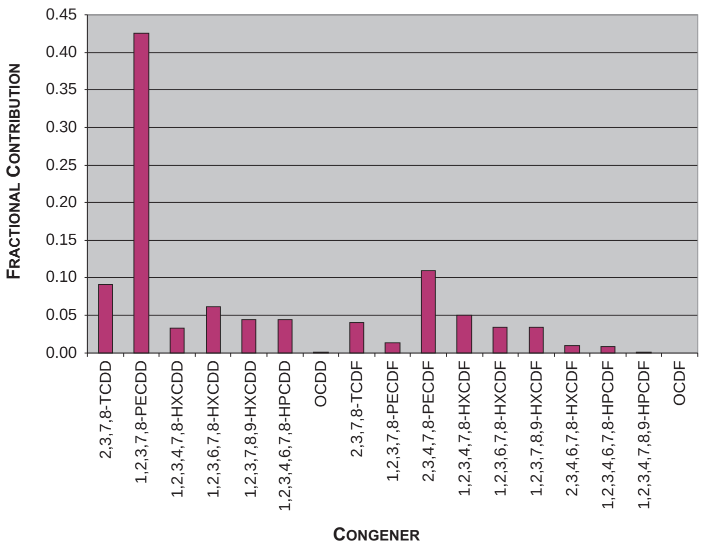

BULK PROFILE **TEQ PROFILE**

Canadian Hog Fuel Boiler 2 - 2007

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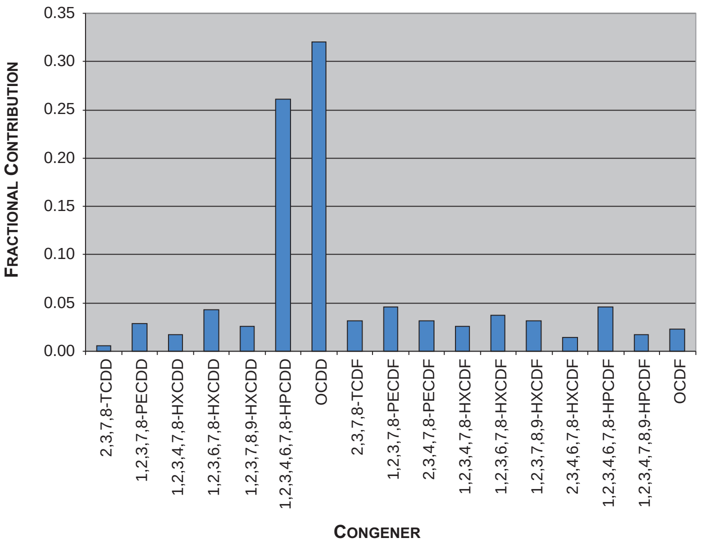

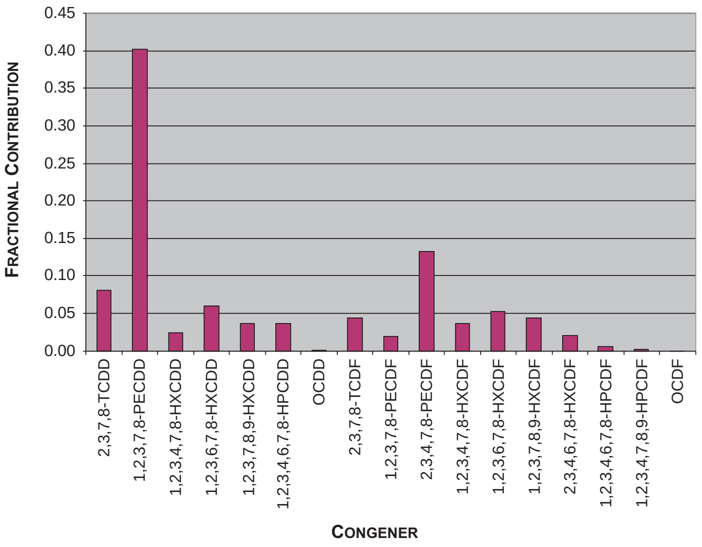

Canadian Hog Fuel Boiler 3 - 2007

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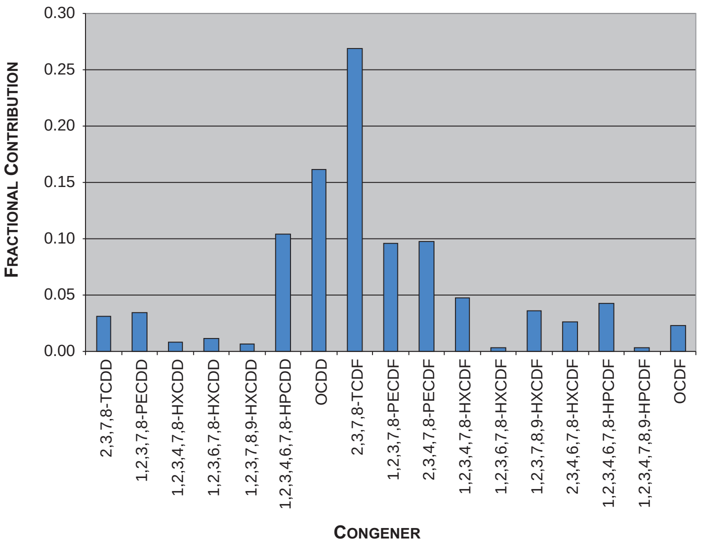

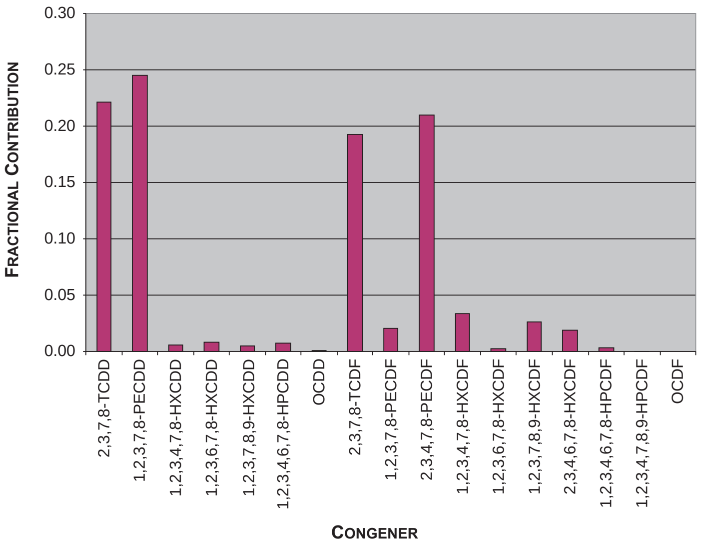

WA Medical Waste Incinerator 1

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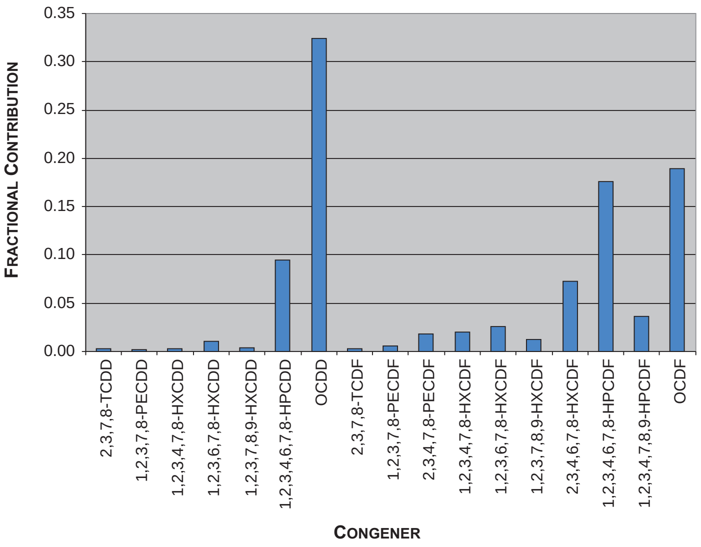

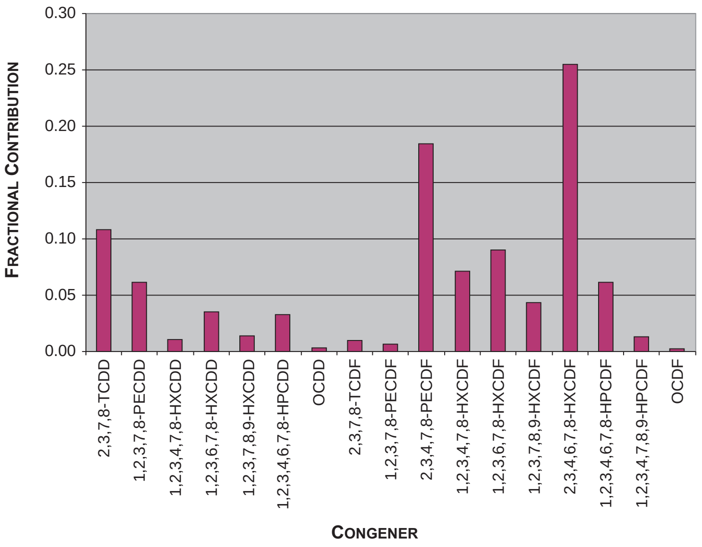

WA Medical Waste Incinerator 2

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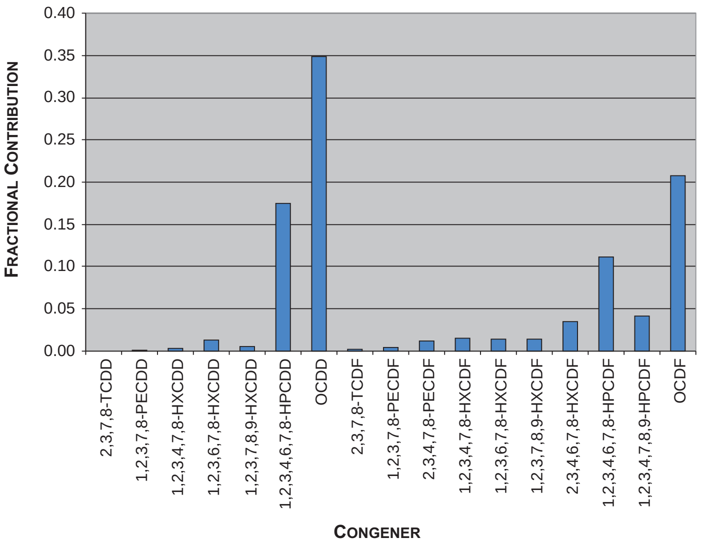

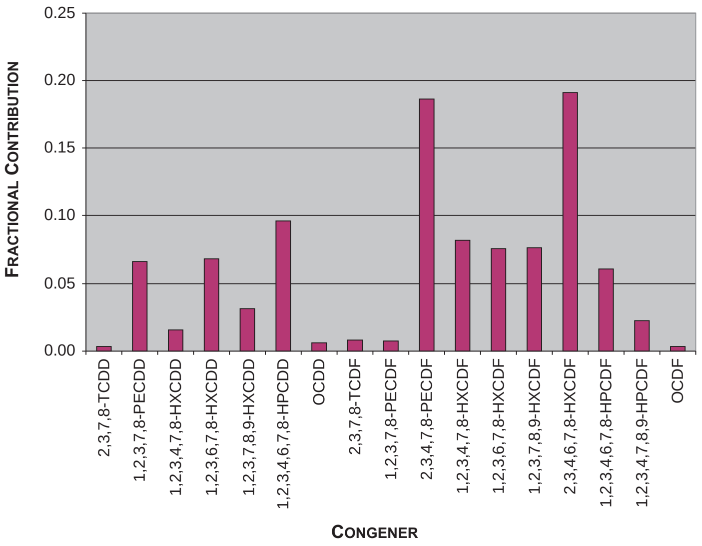

Municipal Waste Incinerator

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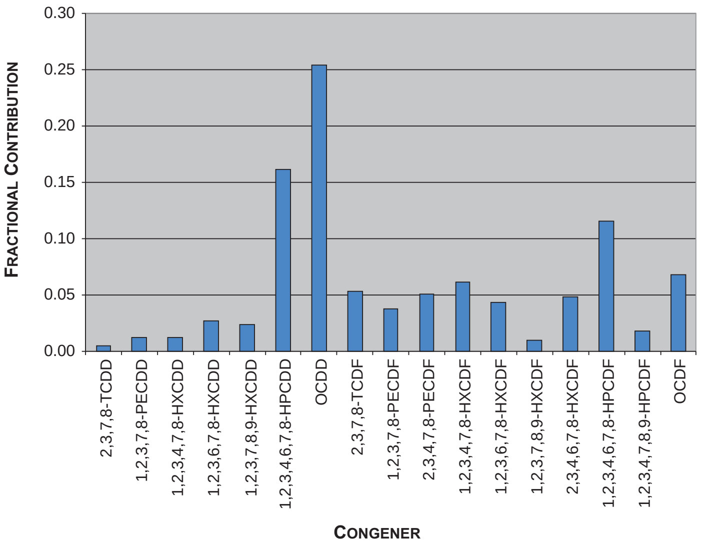

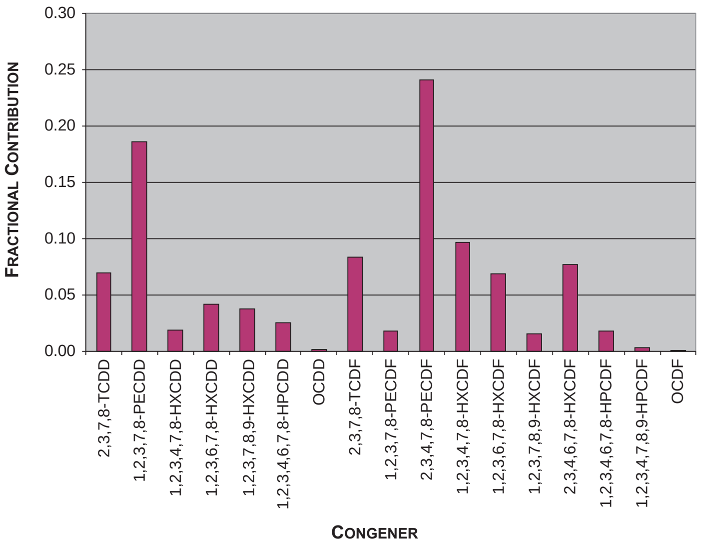

BULK PROFILE **TEQ PROFILE**

Hazardous Waste Incinerator

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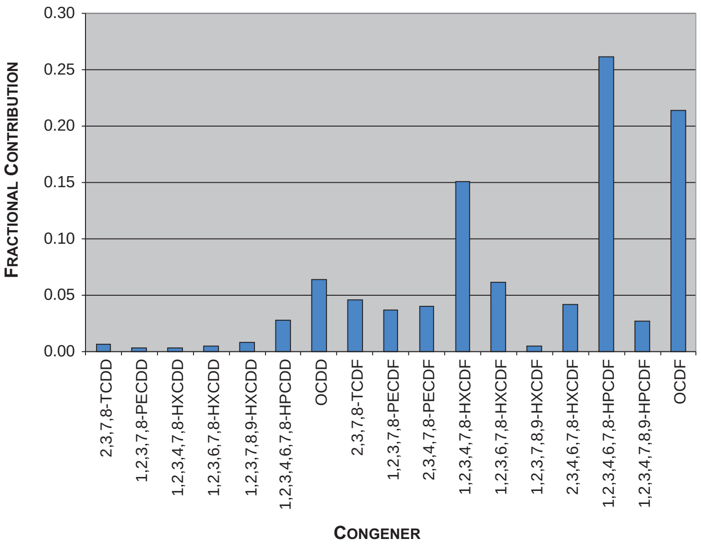

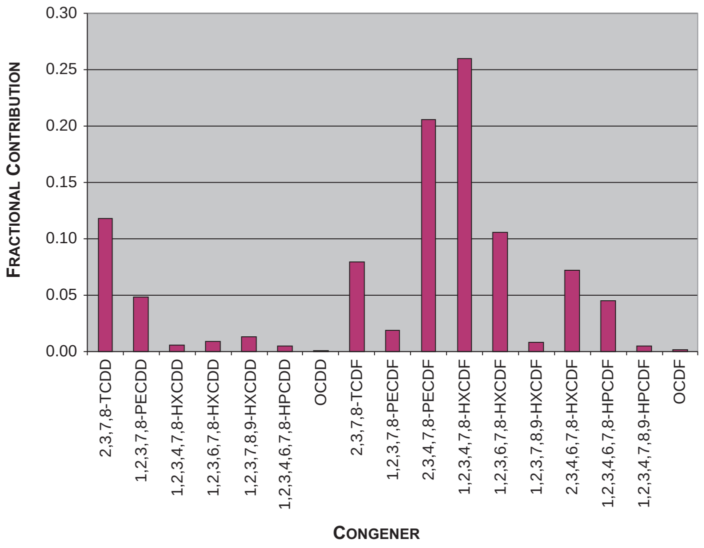

Crematorium

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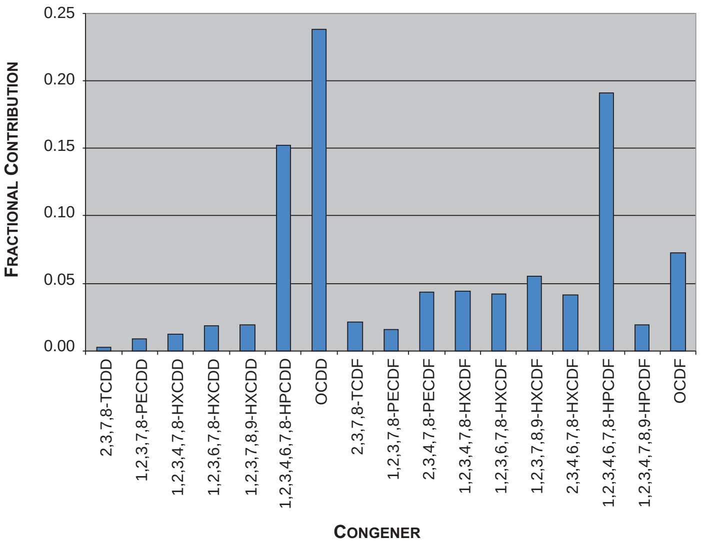

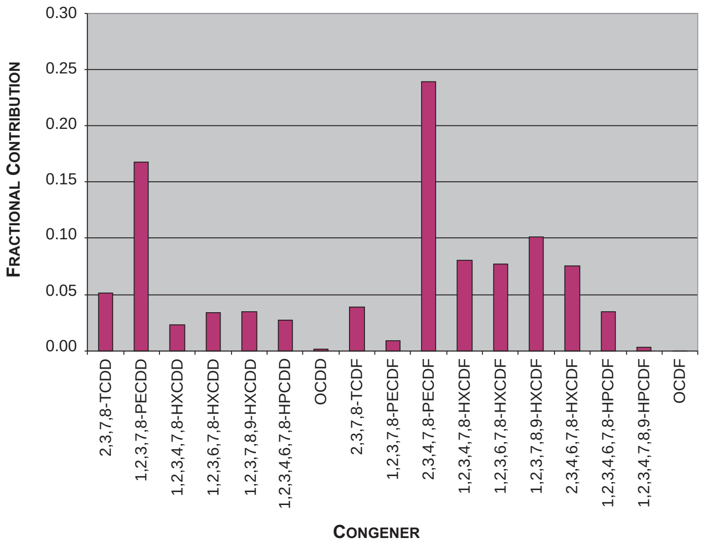

Sewage Sludge Incinerator

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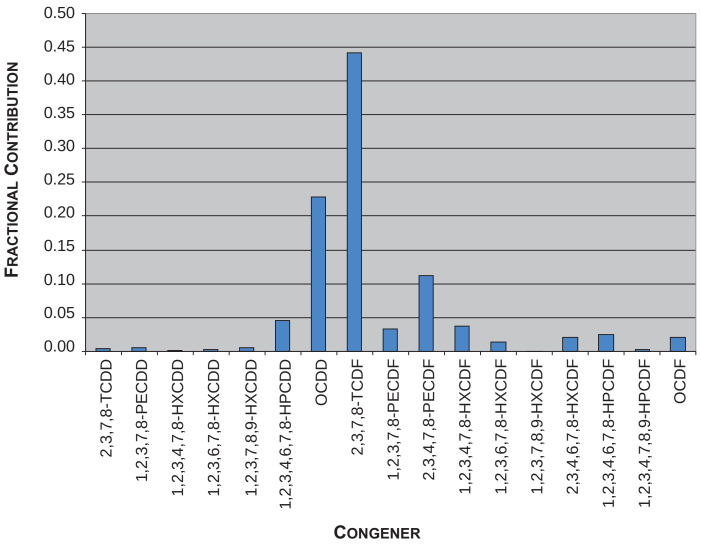

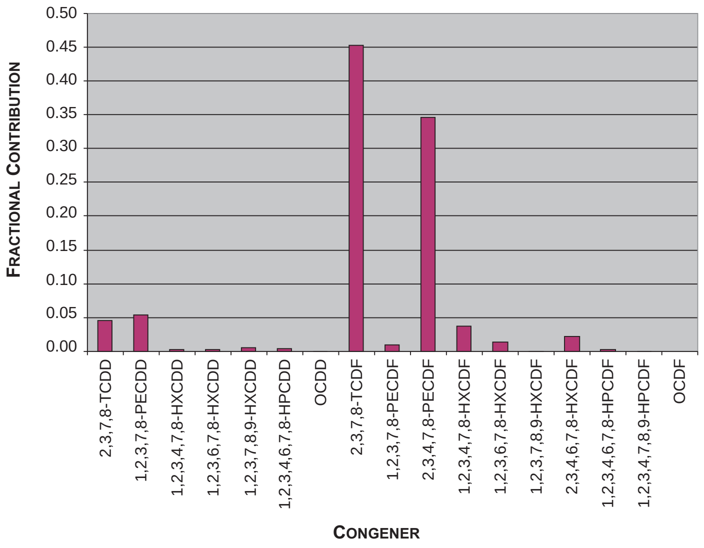

Tire Combustion

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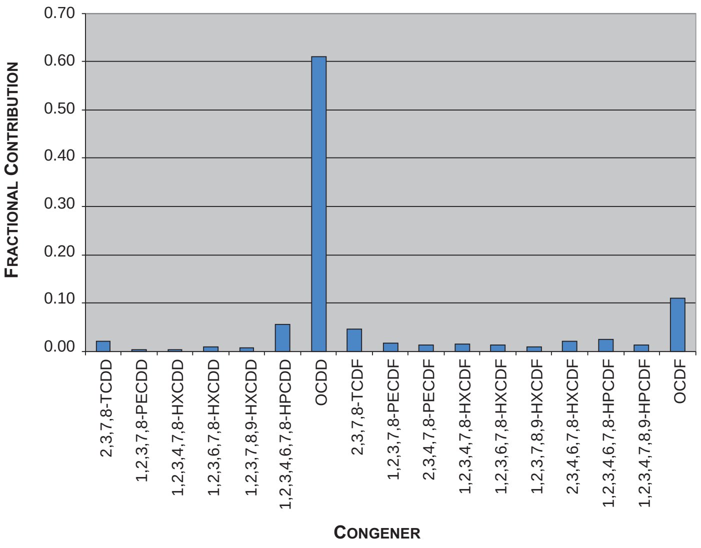

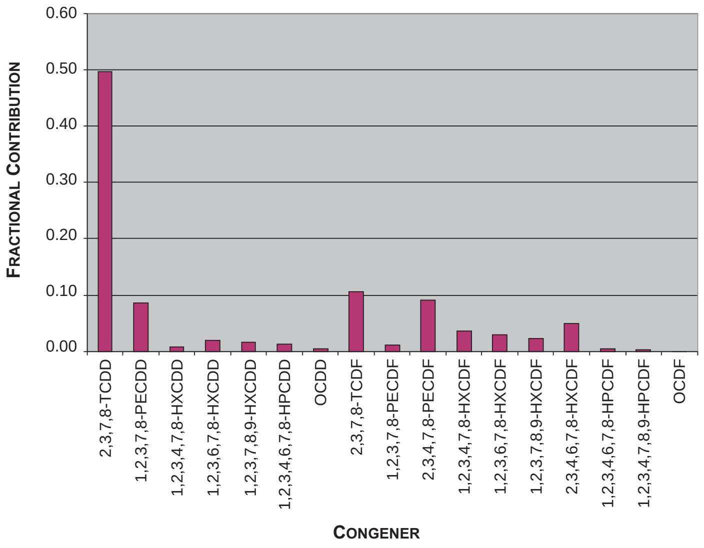

Truck Diesel

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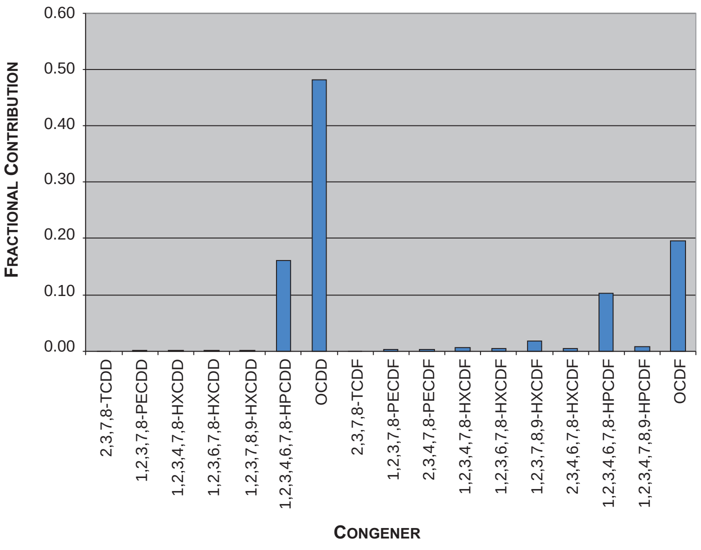

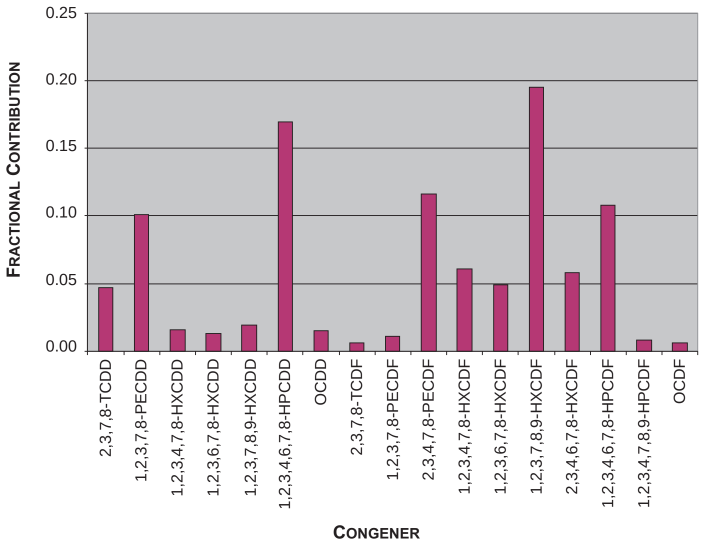

BULK PROFILE **TEQ PROFILE**

Car Leaded Gas

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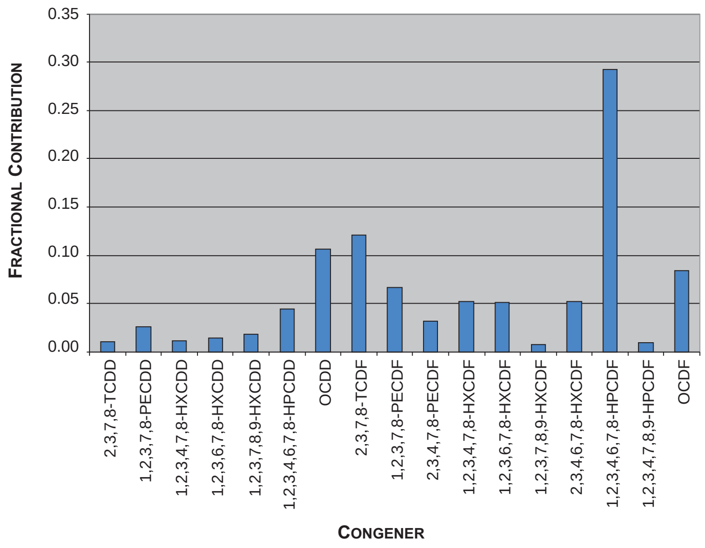

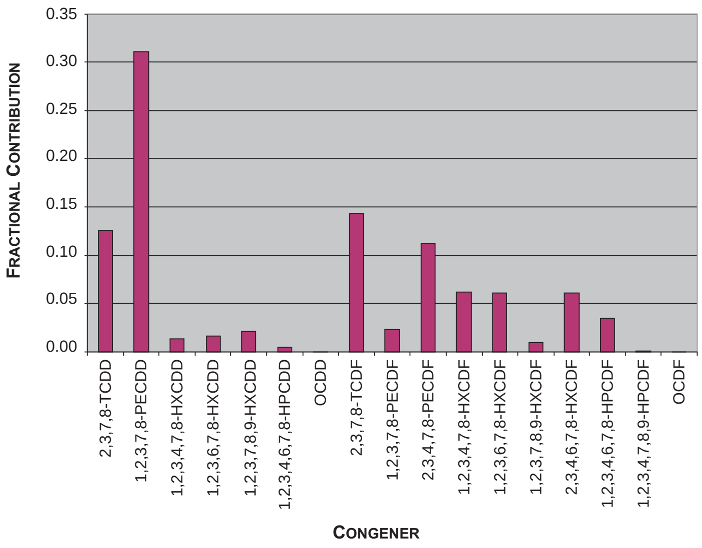

Car Unleaded Gas, Catalytic Converter

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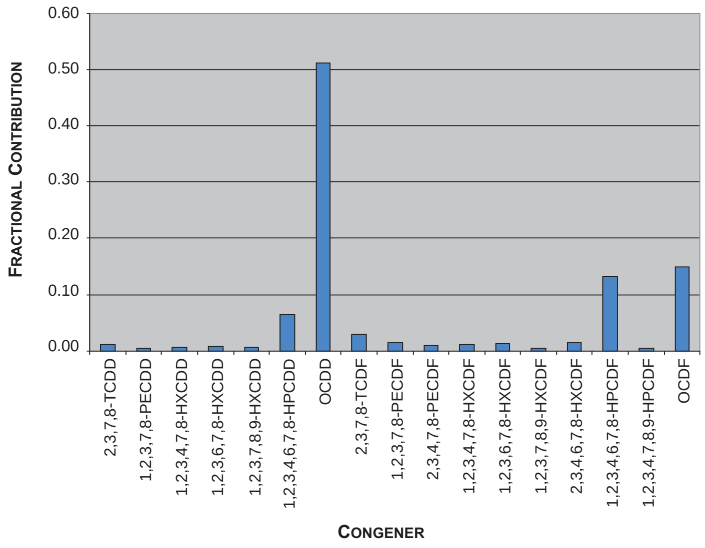

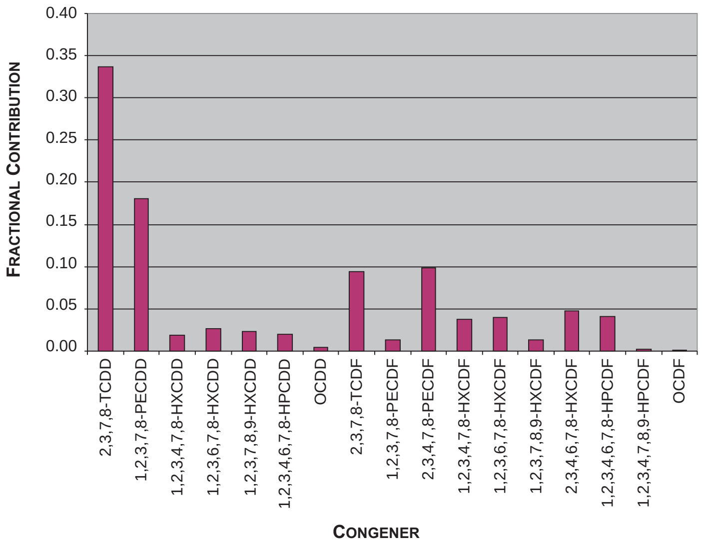

Residential Wood Burning 1

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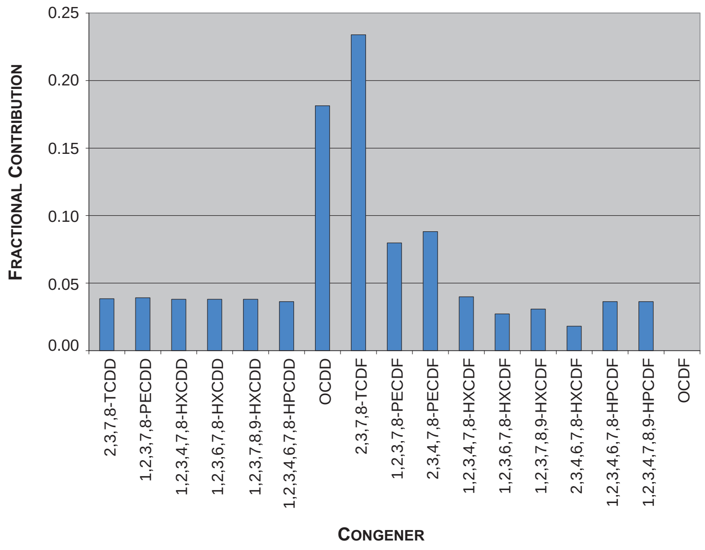

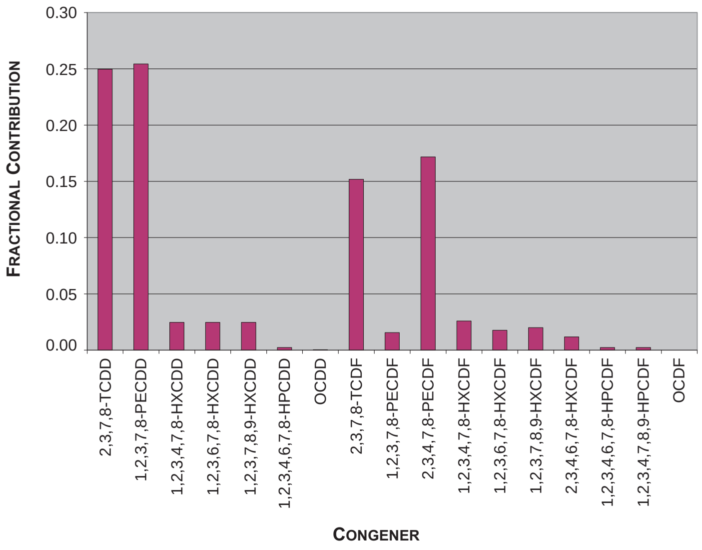

Residential Wood Burning 9

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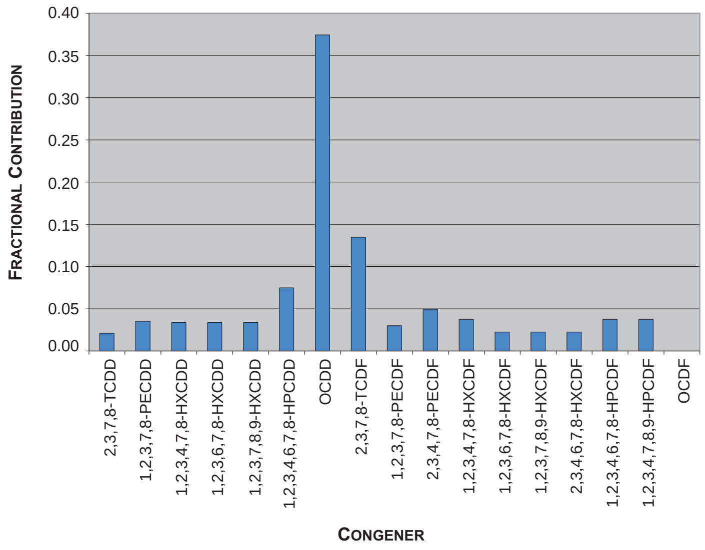

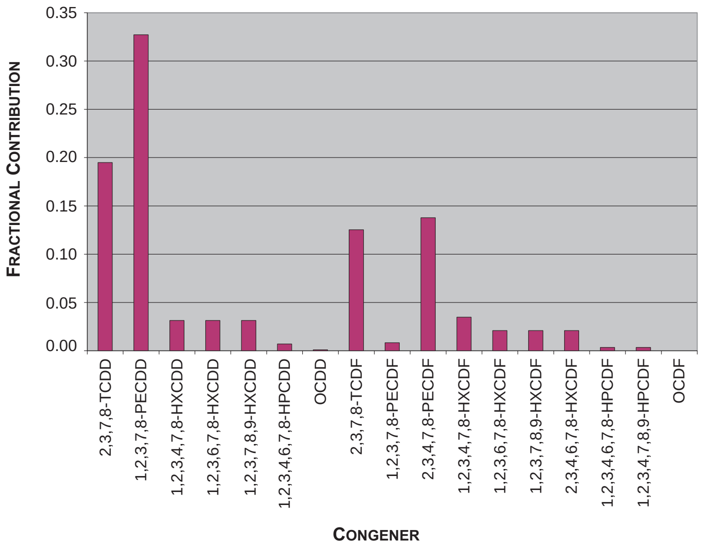

Oil-fired Boiler 1

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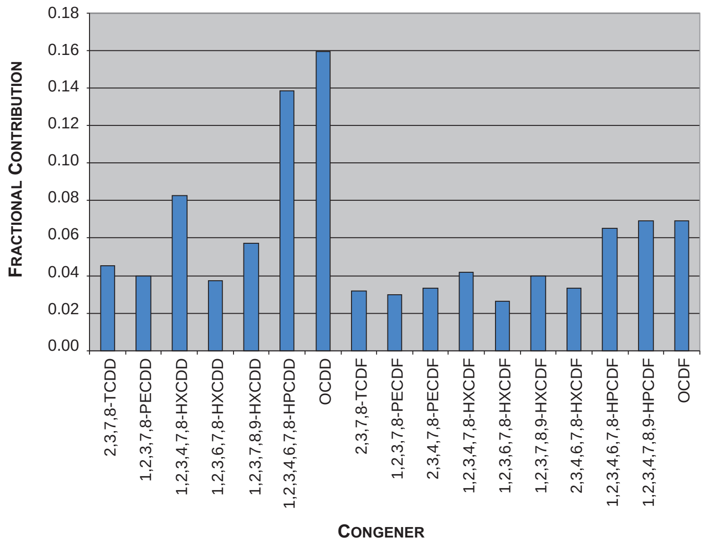

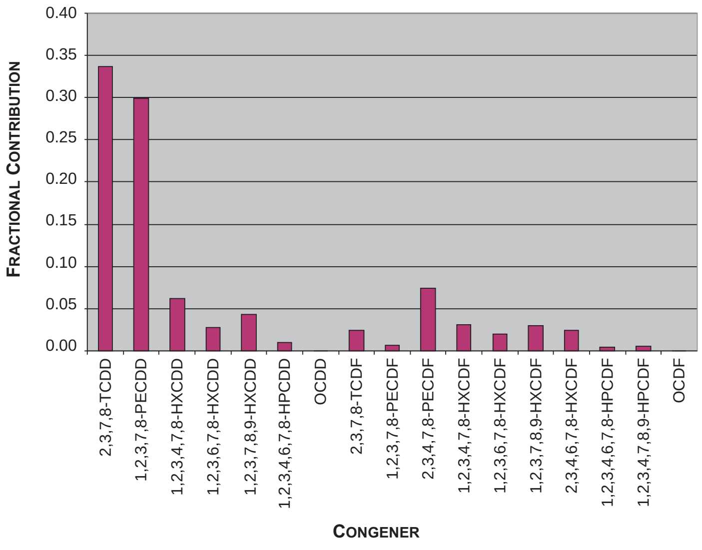

BULK PROFILE

TEQ PROFILE

Oil-fired Boiler 2

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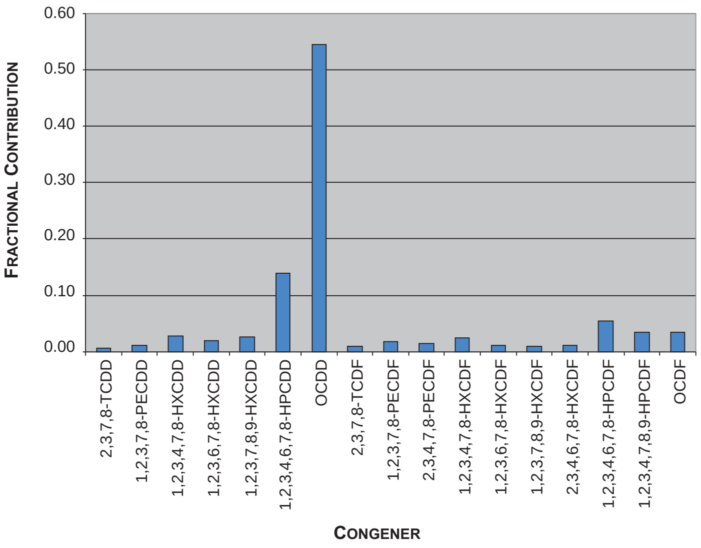

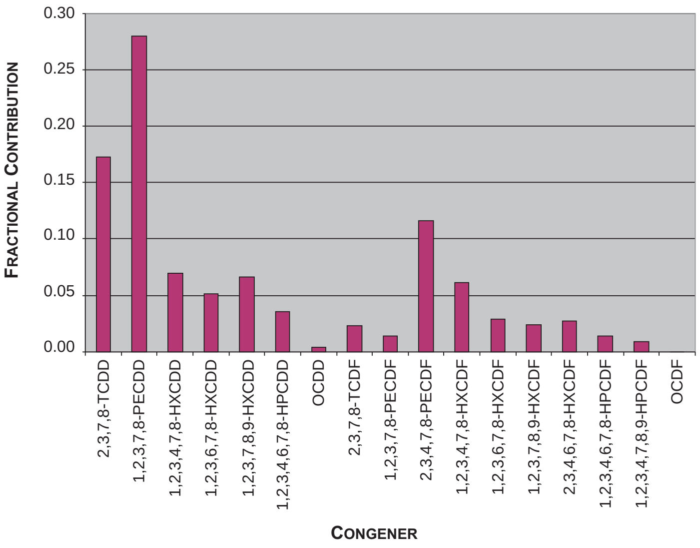

Coal Utility/ Industrial Boiler

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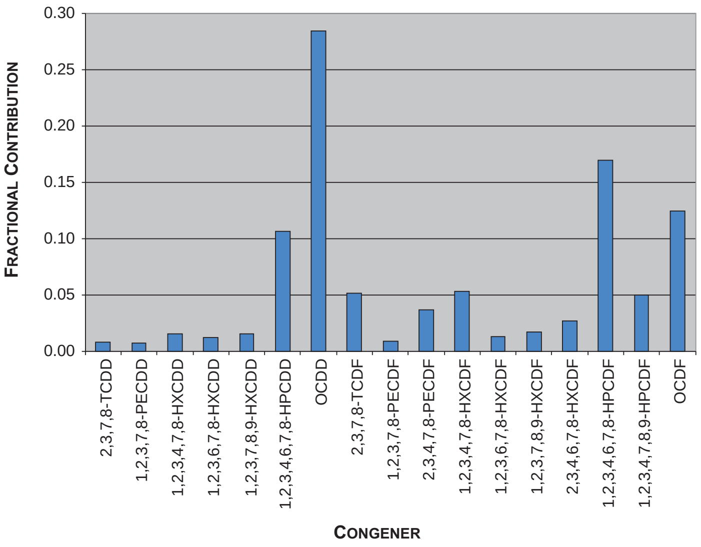

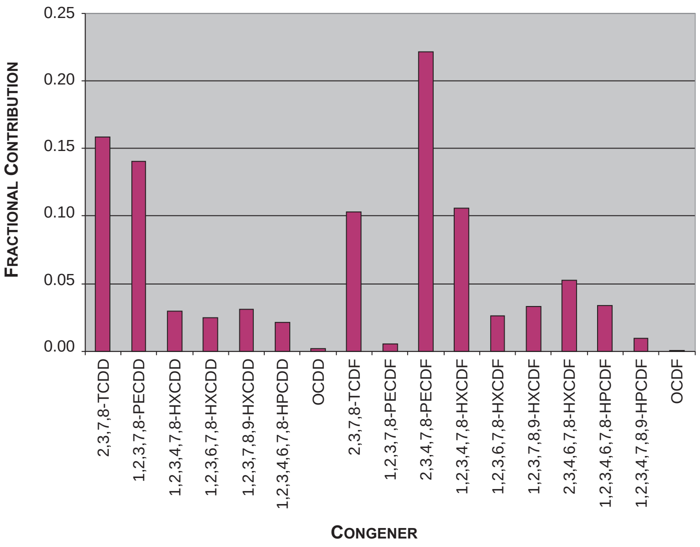

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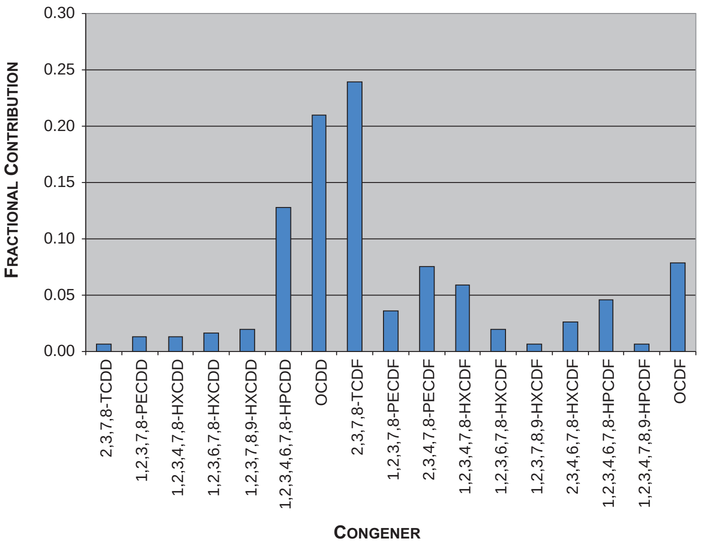

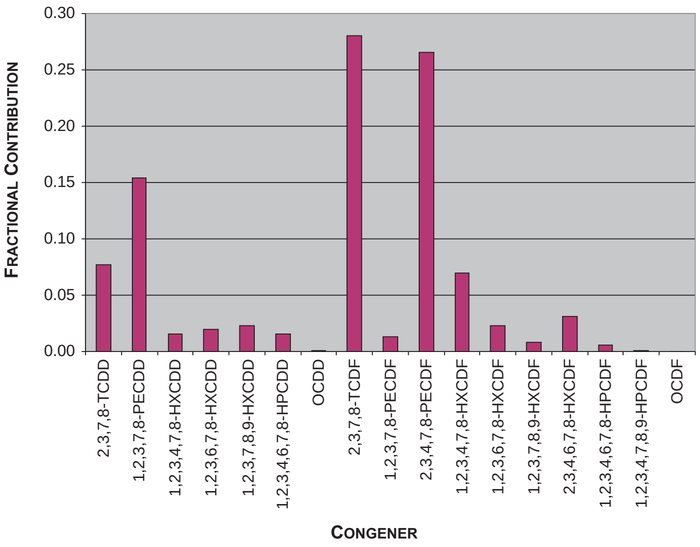

Asphalt Plant

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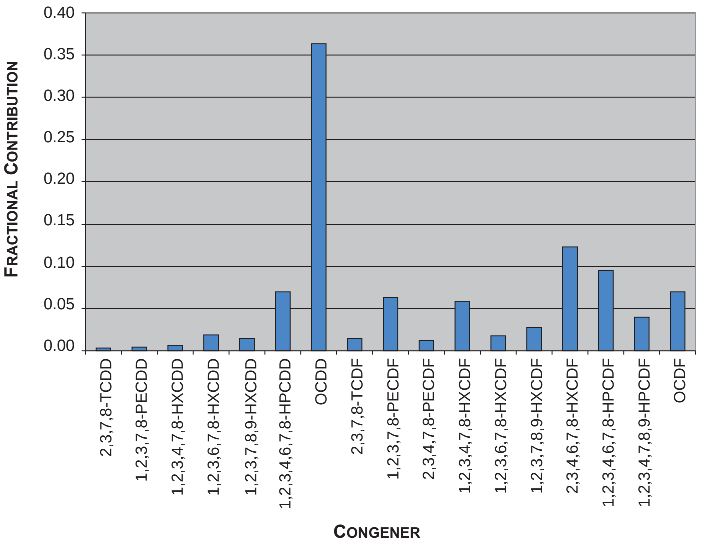

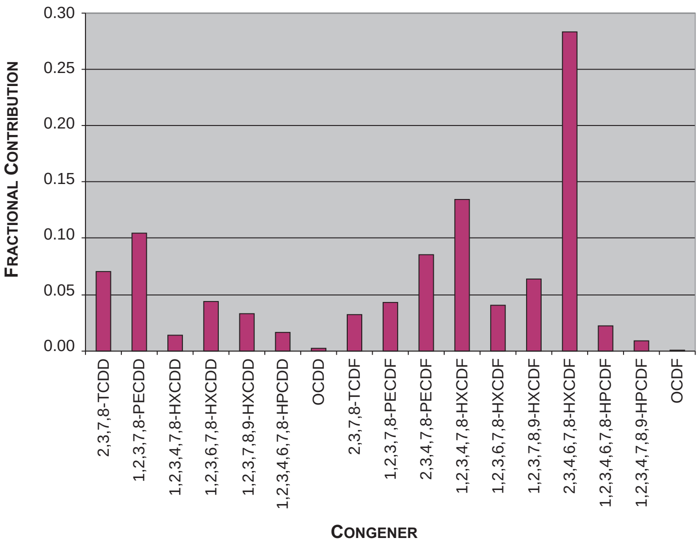

Forest Fire

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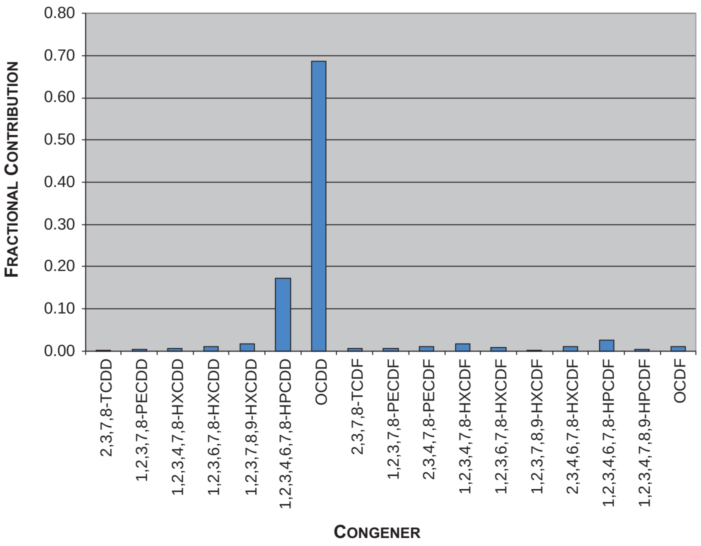

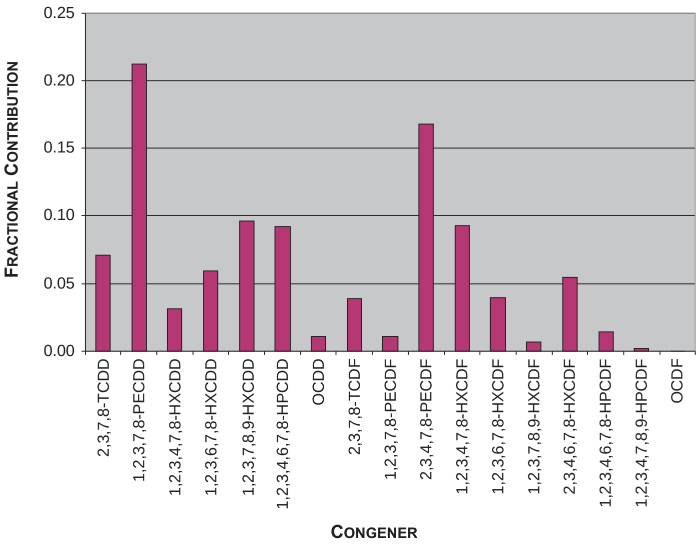

BULK PROFILE

TEQ PROFILE

Household Burn Barrel

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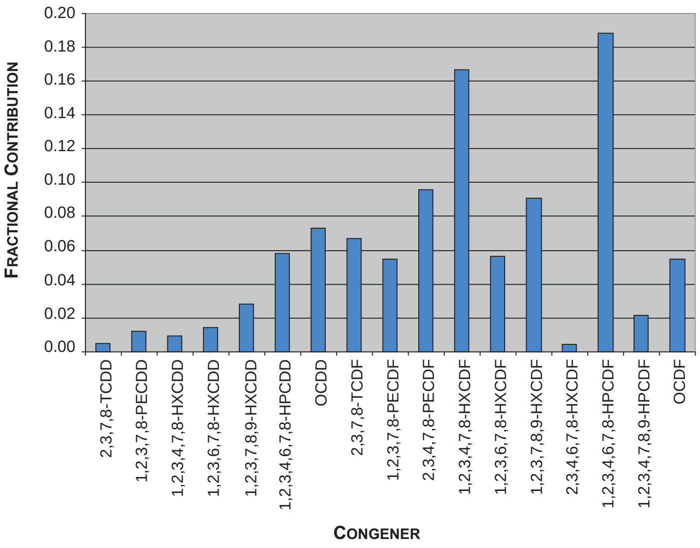

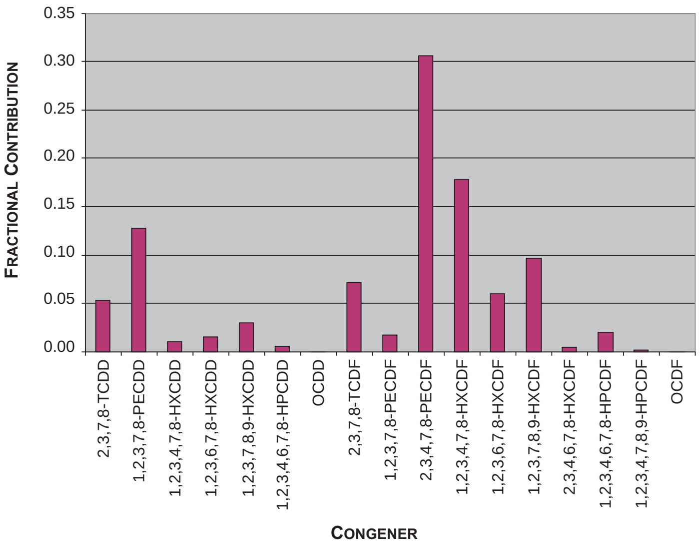

PCB 1248

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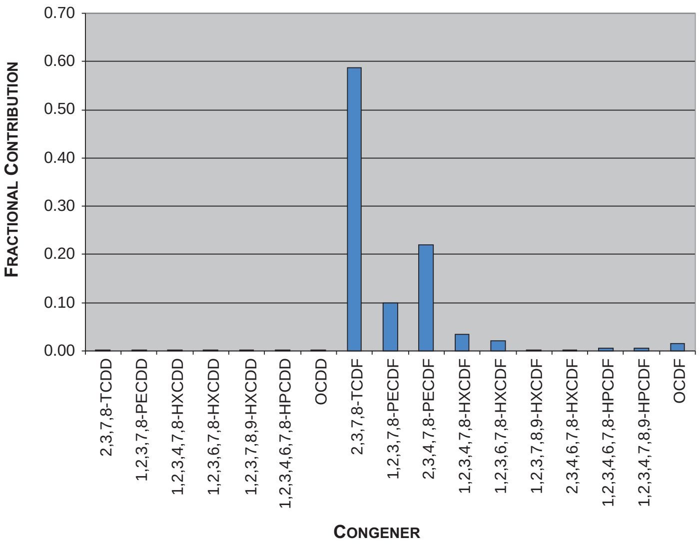

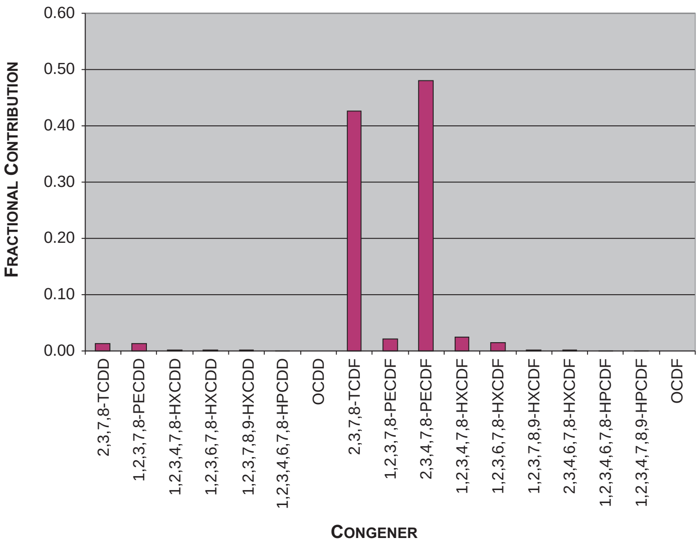

PCB 1254

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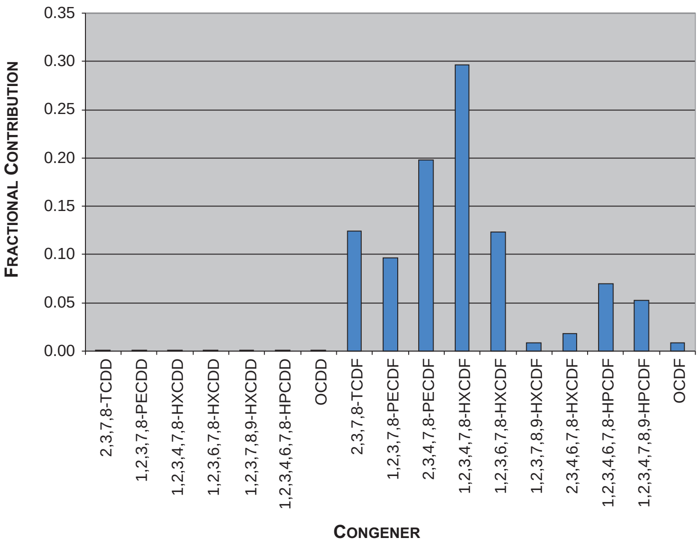

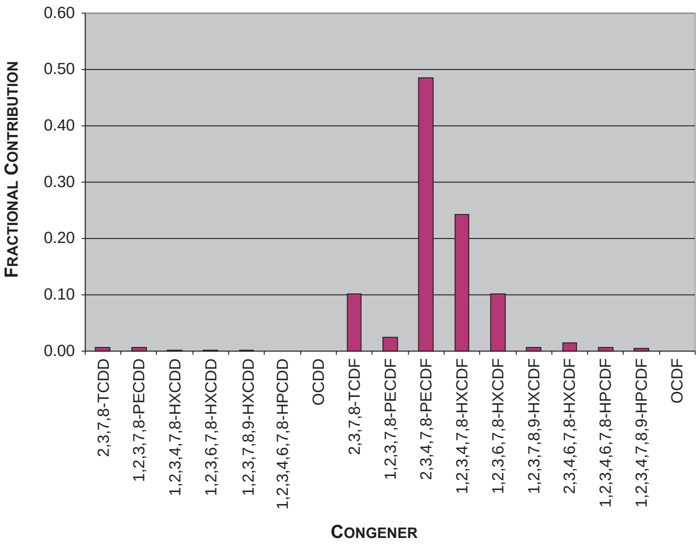

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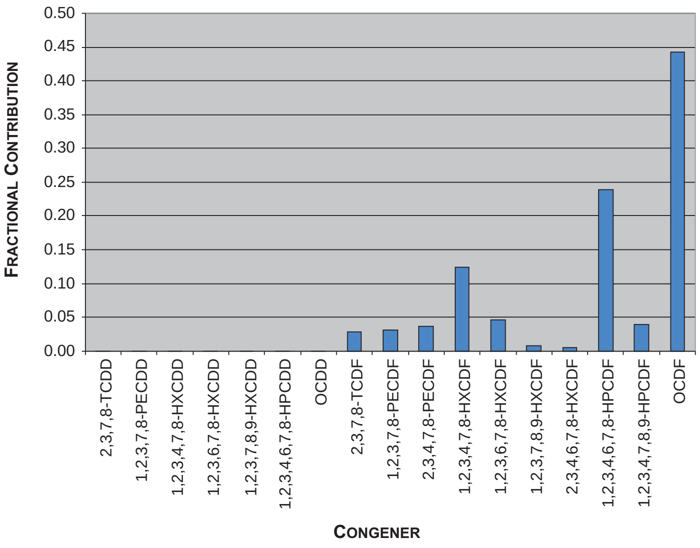

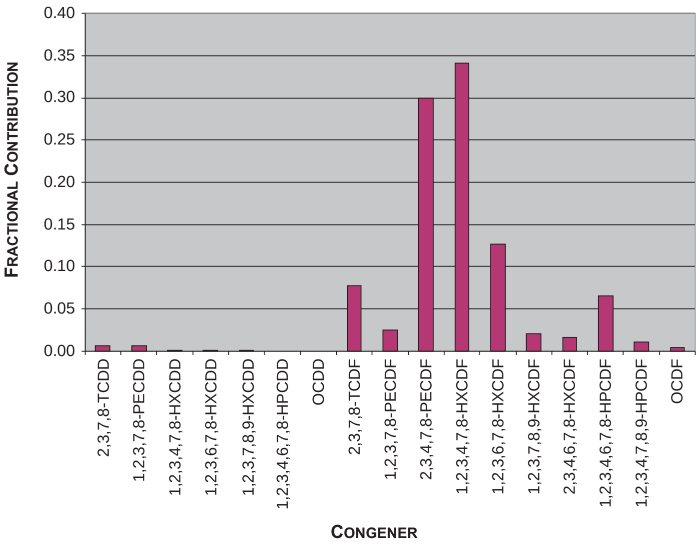

Pentachlorophenol

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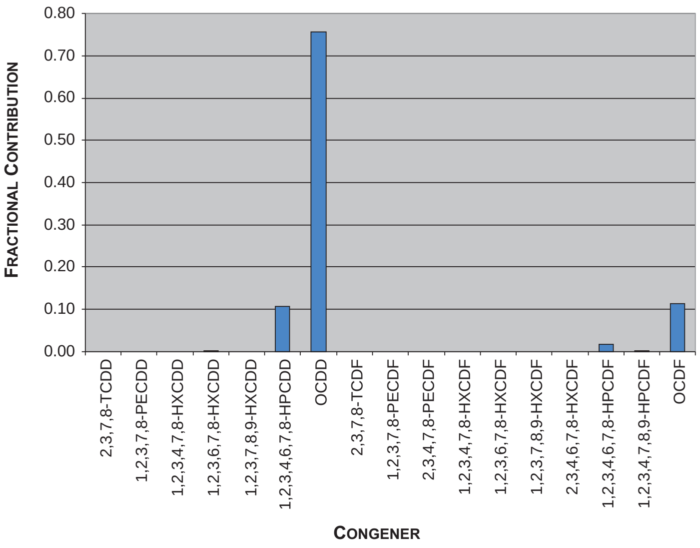

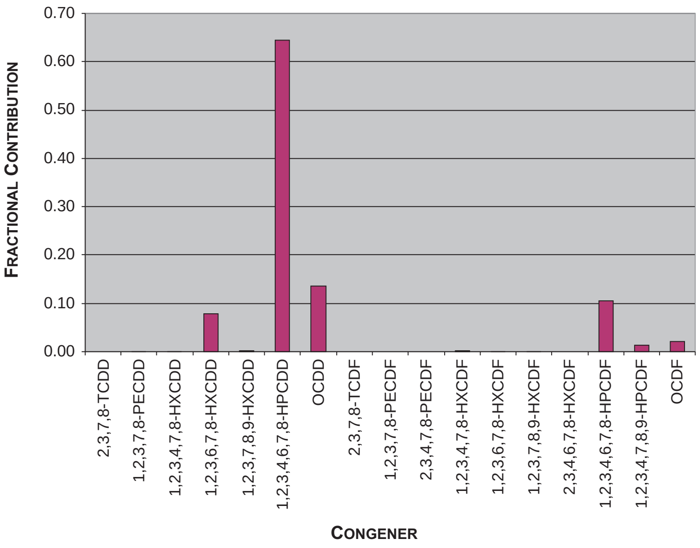

2,4-D

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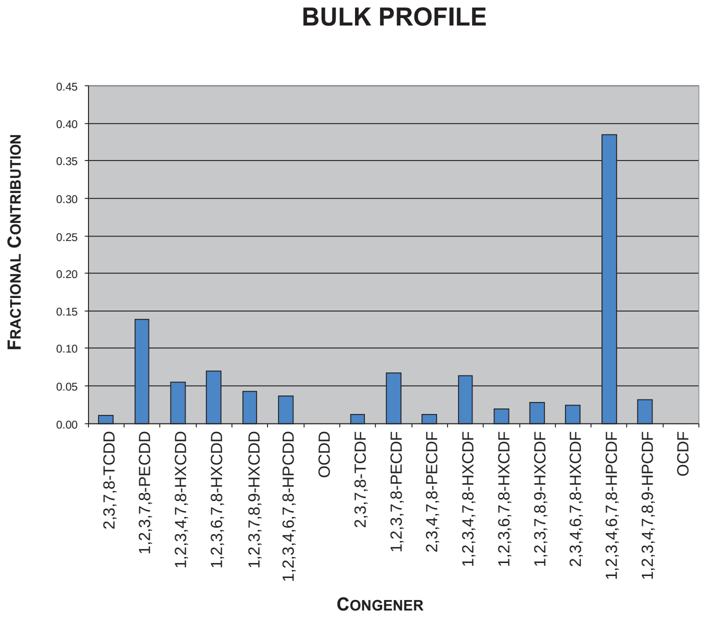

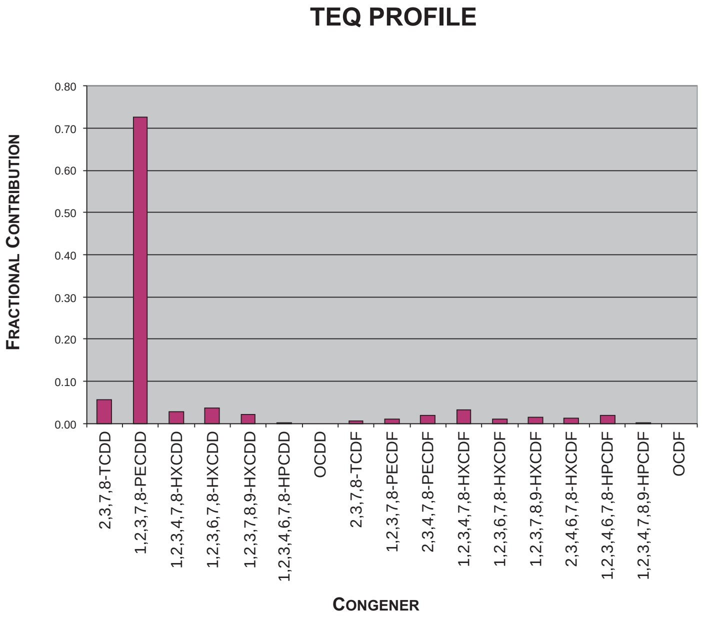

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